

CHEMICAL VAPOR PROCESSING OF CERAMIC COATINGS AND
COMPOSITES

BY

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I dedicate this dissertation to my parents and to the memory of my late great grandmother.

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CHEMICAL VAPOR PROCESSING OF CERAMIC COATINGS AND COMPOSITES

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The chemical vapor deposition (CVD), chemical vapor infiltration (CVI), and atomic layer deposition (ALD) of titanium carbide (TiC_x) coatings onto ceramic substrates and into ceramic fiber preforms were investigated. The purpose of this study was to explore several fundamental and experimental aspects of these processes to improve existing methods of ceramic composite fabrication. A thermodynamic model of TiC_x CVD from TiCl_4 and CH_4 reactants was developed. This model revealed ranges of experimental conditions leading to deposition of either TiC_x , TiC_x + graphite, TiC_x + titanium or graphite. The model also demonstrated that the addition of inlet HCl reduces the extent of TiC_x formation with increasing magnitude as the deposition temperature decreases.

CVD of TiC_x from TiCl_4 and CH_4 reactants onto alumina, graphite, molybdenum, tantalum, silica, and silicon carbide fibers revealed a surface reaction controlled growth

process. As a result, contrasting apparent activation energies, film morphologies, and grain orientations were observed in films grown on these substrates. The dependence of the deposition rate on the reactant concentrations supported the conclusion that a two-site adsorption mechanism governs the deposition process. Furthermore, the injection of HCl into the inlet mixture was found to inhibit the deposition rate.

The CVI of TiC_x was modeled using a single cylindrical pore geometry. The model predictions of the infiltration rate and densification efficiency agreed with general trends found by other models and experiment. Most importantly, the model results showed an improvement in the densification efficiency when a temperature gradient was used in conjunction with HCl injection at the inlet. Infiltrations of Nicalon fiber preforms with TiC_x using a temperature gradient coupled with HCl injection resulted in higher densification efficiency when compared to the same process, except without HCl injection. Composites fabricated using increasing HCl concentrations not only had greater overall density, but also had greater densification uniformity. The improvements in densification efficiency were, however, accompanied by a decrease in the densification rate. ALD TiC_x and TiN resulted in films with significant oxygen contamination due to unidentified leaks in the experimental system.

CHAPTER 1 INTRODUCTION

1.1 Statement of Problem

Both economic promise and technological requirements have motivated the development in recent years of the advanced ceramics [1-3]. These materials possess several superior properties including low density, high hardness, resistance to intense heat and wear, and inertness to oxidation and chemical attack. These qualities allow their tailoring into components that enhance fuel efficiency, increase productivity in industrial processes and replace materials that are scarce or strategic. For instance, ceramic-based automotive engines currently under development are expected to boost fuel efficiency by 30 to 50 percent over conventional engines [4]. Despite the advantages, there is one fundamental limitation to the widespread use of these materials: their brittleness [5,6]. The combination of ionic and covalent atomic bonding which endows ceramic materials with the aforementioned beneficial properties also translates into an inherently low resistance to crack propagation (low fracture toughness). As a result, ceramics tend to fail catastrophically when cracks develop from small defects and propagate due to stress. While the critical fracture toughness of most metal alloys is in the range of 30 to 50 $\text{Mpa}\cdot\text{m}^{1/2}$, ceramics have fracture toughness values of only 0.5 to 6 $\text{Mpa}\cdot\text{m}^{1/2}$ [5].

The solution of this problem has led to the evolution of a class of materials called ceramic matrix composites (CMCs) [1,2,7-9]. By adding a secondary phase (reinforcing

phase) to the primary ceramic body (matrix), improvements in fracture toughness as well as in the magnetic, electrical, and thermal properties are achieved. Advances in the field of composites in the last two decades, for instance, have increased the fracture toughness of ceramics to values of 20 to 30 Mpa-m^{1/2} [10-15]. Typical reinforcing phases can be in the form of fibers, whiskers or dispersions of another material [9,16-20].

The use of these hybrid materials allows greater flexibility in design because of the wider range of property variation obtained by combining different constituents. The mechanical properties of CMCs are, however, significantly influenced by the mechanical properties at the interface of the composite constituents [21]. Figure 1.1 illustrates the stress-strain behavior of a fiber-reinforced ceramic matrix composite under tensile load. By a suitable combination of interfacial bonding, fiber strength, and residual stresses due to contraction of the fibers and matrix upon cooling, a non-catastrophic mode of failure can be achieved. Qualitatively, this failure mechanism is found in composites with weak bonding at the interface (weak interface), high strength fibers, and tensile residual stresses normal to the fiber/matrix interface [22,23]. Departure from these parameters, particularly strong interfaces, leads to a catastrophic mechanism characterized by a linear stress-strain curve to failure. Thus, the need to control the properties at the interface is an overriding factor in the selection of materials and processing techniques for composite fabrication.

The use of vapor processing techniques in the fields of ceramic and ceramic composite fabrication has grown rapidly in recent years. Benefiting from over thirty years of application in the microelectronics industry, the process of chemical vapor deposition (CVD) has been successfully expanded to many areas of ceramics processing. The

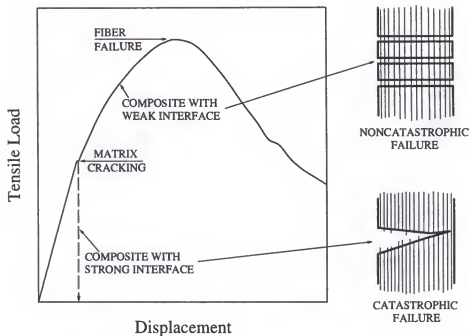


Figure 1.1 Schematic tensile stress-strain behavior of ceramic composites [22].

technique has been used to produce high performance ceramic tool bits, protective coatings against oxidation and wear, and fiber-reinforced ceramic matrix composites [24-35]. As in most microelectronics applications, the use of CVD in ceramics processing involves the reaction of vapor phase precursors to deposit a solid film onto the external surfaces of a substrate material. The extension of CVD to the fabrication of fiber-reinforced ceramic matrix composites, however, creates the added complication of having to deposit the ceramic matrix within the porous structure of an array of fibers or whiskers (preform).

Appropriately, the application of CVD to composites processing has been named chemical vapor infiltration (CVI) to emphasize that deposition occurs on the internal surfaces of the preform [11,30,36]. In CVI, the reinforcing phase is incorporated into the ceramic matrix by infiltrating and densifying the porosity within the preform with the

matrix material. Several advantages make CVI an attractive choice for composite fabrication. Because CVI and CVD require similar processing equipment, several steps of composite processing can be accomplished in the same processing unit [1,21,30]. For instance, prior to infiltration, the fibers in the preform can receive a precoating essential to protect the fibers or to modify the fiber/matrix interface properties. These steps can be easily performed by simply changing reactants, while using the same equipment. Second, CVI generally utilizes lower processing temperatures which produces lower residual stresses than other ceramic consolidation techniques, thus, minimizing damage to the reinforcing phase [5,11,16,37]. Another advantage of CVI is that it can be used to fabricate irregularly shaped components [34,35]. Finally, the ability to deposit a solid material from gaseous molecular building blocks allows CVI to create fine grained coatings and ceramic matrices of superior purity and better controlled microstructure and composition than other fabrication methods [5,11]. This ability is of particular importance in tailoring the properties at the matrix/reinforcement interface and results in enhanced low and high temperature composite performance.

The versatility of CVI has been demonstrated with different composite systems. Matrices deposited include: Carbon, SiC, CrC, TiC, B₄C, TaC, ZrC, Si₃N₄, BN, TiB₂, ZrO₂, and Al₂O₃ [3,10,11,15,35,38-85]. Fibers based on Carbon, SiC, TiC, Si₃N₄, BN, Al₂O₃, and SiO₂ are examples of reinforcing materials [11,12,41,47-55,59,60,63,79-81,84,86,87]. Composites made by CVI have applicability in turbine and automotive engine components, advanced structures for hypersonic aircraft and spacecraft, heat exchangers operating at temperatures greater than 1000 °C and under corrosive flue environments, energy saving cogeneration systems such as combustion thermionic

converters, and radiation absorbing wall materials for fusion reactors [2,7,8,20,30,33-35,88].

Most commercial CVI processes are isothermal and require the gases to diffuse into a free-standing fibrous preform. These processes, called isothermal isobaric CVI (ICVI), are well suited for fabrication of thin-walled composites of any shape [3,15,21,62,69,70]. The reliance on diffusion to transport the reactants into the interior of the preform and the fact that operating conditions necessary for thorough densification inhibit fast deposition of the matrix, however, make ICVI an inherently slow process. As a result, it often takes weeks to months to achieve sufficient densification [62,70,89]. Consequently, other variations of CVI have been developed which incorporate thermal and/or pressure gradients or reactant pulses [30,36]. The most promising of these modifications has been the Oak Ridge National Laboratory (ORNL) process, called forced-flow temperature gradient CVI (FCVI) [13,67,76]. It utilizes opposing thermal and pressure gradients to speed densification. Infiltration times are reduced from weeks to less than 24 hours for composite specimens 25 mm thick which show no significant density gradients between the surface and the interior [76,81]. Nevertheless, because special fixtures are required, only composites of simple shape can be processed. The research effort in FCVI has involved Carbon-Carbon, SiC-Carbon, and more recently SiC-SiC composites, but little work has been reported in other systems [3,15,21,44-46,49,53,62,69-73,76,79,80,87,89-91].

The focus of this dissertation is to investigate the use of vapor processing techniques (i.e., CVD and CVI) to fabricate Nicalon fiber-reinforced Titanium Carbide (TiC) matrix composites. Specifically, this work has concentrated on improving the

FCVI process by exploiting the reversibility of the chloride chemistry used to deposit the TiC matrix. The inhibiting effect of HCl, a reaction by-product, on both the deposition kinetics and thermodynamics driving force coupled with the temperature gradient allows better control over the infiltration process, thus reducing density gradients in the composite. To better understand this novel CVI process a reaction equilibrium model of TiC deposition and a detailed model of infiltration of single pores are developed. It is anticipated that this approach can be applied to other matrix/reinforcement systems and the results of this work will provide fundamental insights in the fabrication of composite materials.

1.2 Overview of the Literature

1.2.1 Titanium Carbide and Titanium Carbide CVD

Titanium carbide (TiC) is a transition metal (group IVB) refractory carbide. Its stable room temperature phase is of the cubic NaCl (fcc, B1) type with the smaller C atoms occupying the octahedral interstices of the parent fcc-Ti lattice [92,93]. These octahedral sites can also be host to impurities such as H, N, and O [94]. TiC, as other refractory compounds with NaCl-type structure, exhibits a strong tendency for octahedral site vacancy formation, which leads to a broad range of homogeneity (~16%) [95,96]. Consequently, TiC is more accurately represented by the symbology TiC_x where x stands for the ratio of carbon to titanium atoms. For instance, at 1900 K, the composition range of TiC_x ranges from $x=0.49$ to $x=0.96$ [96]. This variability in stoichiometry means that a wide spectrum of physicochemical properties of TiC_x is accessible, thus making it possible to use composition to tailor specific properties.

The technological importance of TiC_x is evidenced by its properties. It is one of the hardest materials known (9-10 Mohs), having a remarkable thermal stability (maximum melting temperature of 3067°C at $x \approx 0.8$) and inertness to acids and alkalis [94,97,98]. In addition, TiC_x has an excellent resistance to wear, exhibits plastic deformation behavior (similar to fcc metals) above 800°C , and has low friction coefficients against unlubricated metals such as Ni, Al, and Fe [95,99-102]. These mechanical properties along with a strong adhesion to metal and carbide substrates have resulted in numerous applications of TiC_x since the early part of this century. Applications include protective coatings for steels, cemented carbides, and cermets used for cutting and milling tools, cold extrusion nozzles and punches, and forming and stamping articles [27-29,99,102-109]. Furthermore, TiC_x is used in low-friction coatings for bearings and has been considered as a low-friction thermal barrier in cylinder walls of adiabatic diesel engines [110,111]. Because of its excellent high temperature properties and low physical sputtering yield, TiC_x is also the leading material for proposed first-wall components of fusion reactors [112-114]. More recently, TiC_x has been studied as a high temperature oxidation resistant coating and matrix material for ceramic matrix composites [52,55,62,78,84,85,115,116].

With the explosion of semiconductor industry, the electromagnetic properties of TiC_x have also drawn attention. TiC_x has a near-metallic electrical resistivity ($35\text{-}250\ \mu\Omega\text{-cm}$) and becomes superconducting below $4.2\ \text{K}$ [117,118]. The dependence of optoelectronic properties of TiC_x with composition and the calculation of its electronic band structure have been reported by several authors [92,117,119-123]. Semiconducting films of TiC_x have been obtained on silica substrates [124]. So far, TiC_x has been used in

MOSFET gate electrodes, as diffusion barrier in integrated circuit metallization schemes, and as a substrate for other wide band gap, refractory materials such as diamond, cubic boron nitride, and silicon carbide [125-128]. A broader list of property values of TiC_x as well as their dependence on composition can be found in several reviews and texts on carbides and transition metal refractory compounds [93,94,98,129-131].

One of the first techniques used to make TiC_x was its isolation from titanium-bearing cast iron. Today, bulk TiC_x is produced industrially by the reduction of TiO_2 at 1500 to 2000 °C with carbon black, a process used since the turn of the century [94]. This technique normally results in a mixture of lower oxides of titanium surrounding a TiC_x core. The TiC_x product is invariably contaminated with O and N, and is deficient in carbon. TiC_x has also been prepared by the reduction of TiS_2 and TiH_4 with carbon [7]. The latter, when carried out under vacuum at 1200 °C results in a near stoichiometric product after one hour. Other carbon reduction techniques include the use perovskite (CaTiO_3) or ilmenite concentrate at 1400 to 1800 °C [132]. The direct reaction of the elements, either in an arc furnace, or as sintered powders, has also been investigated to obtain oxygen free TiC_x [5]. Because of limitations imposed by the diffusion of carbon through TiC_x , this process is considerably slow, but a pure carbide can be obtained if sufficient vacuum is used. The reaction of alkali metal chlorides with titanium-bearing ores is another technique that has been used to increase purity [133]. The ore is reacted with the metal chloride and a carbonaceous material at 2200 °C, resulting in pure TiC_x after acid-leaching. In an alternative route, CaC_2 and TiCl_4 are reacted at 800 °C to form TiC_x and by-products CaCl_2 and HCl [5]. A water wash releases the TiC_x from CaCl_2

and unreacted CaC_2 . If CaC_2 is free from oxides or hydroxides, pure TiC_x can be obtained.

The history of CVD of TiC_x dates back to the last decade of the 19th century, when Erlwein proposed the deposition of TiC_x onto glowing lamp filaments by reacting volatile metal compounds with hydrocarbons diluted in hydrogen [134]. The first detailed study of the necessary deposition parameters and properties of the resulting coatings was published by van Arkel [135]. By the end of World War II, only a few publications had appeared describing deposition conditions and the relationship between these parameters and the quality of the deposits [136-137]. A threshold temperature of 1200 °C had been estimated for deposition of TiC_x from volatile hydrocarbons compounds and the co-deposition of undesirable carbon had also been reported. To avoid carbon co-deposition, van Arkel used carbon monoxide instead of a hydrocarbon source, but it is speculated the TiC_x deposits were contaminated with oxygen [136]. The application of TiC_x as a protective coating was not considered seriously until the work by Campbell et al. in 1949 [138]. Until then, it was believed the elevated temperature required to deposit the coatings would damage steel tools and that their use would be limited due to the brittleness of TiC_x . The first report of successful use of TiC_x protective coatings was made in 1953 by the metallurgical laboratory of Metallgesellschaft AG in Germany [139]. This led to a patent in 1960 and licensing worldwide.

Since then, CVD of TiC_x for various applications has been researched extensively. Many of these studies have addressed deposition on steels as well as WC-Co and WC-TiC-TaC-Co cemented carbides and $\text{TiC}(\text{TiCN})$ -Ni-Mo cermets. These investigations have shown that the nature of the substrate plays a noticeable role in the CVD process

[24-29,102,106-108,140-153]. This influence has been attributed to the catalytic activity of the Fe-group metals in the substrate on the cracking of the hydrocarbon species, a process which continues as the coatings grows due to diffusion of metal atoms into the TiC_x layer [154].

Traditionally, TiCl_4 , CH_4 , and H_2 mixtures have been used as reactants for TiC_x CVD, but other carbon sources such as C_2H_4 , C_3H_8 , C_2H_2 , C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, CCl_4 , and CO_2 have also been investigated [24,102,104-108,113,136-138,142-144,155]. In some cases, the carbon present in the substrate is a sufficient source for TiC_x formation [156-158]. TiC_x deposition on carbon containing substrates has, however, invariably led to the formation of a decarburized interface (eta-layer) which affects adhesion and other properties of the TiC_x coating [159-161].

Several authors have discussed the deposition kinetics of TiC_x CVD, but all of these reports cover only a narrow range of deposition parameters and do not attempt to isolate the surface phenomena from mass transfer effects [102,107,108,142,162]. Recently, Haupfear and Schmidt have shown, using in-situ gravimetric techniques, that a one site competitive adsorption mechanism governs the kinetics of TiC_x deposition from TiCl_4 - C_3H_8 - H_2 precursors [163]. The equilibrium of the Ti-C-H-Cl system resulting from TiCl_4 - CH_4 - H_2 , TiCl_4 - CCl_4 - H_2 , and dichlorotitanocene- H_2 chemistries has also been reported in various papers [157,164-169]. These studies have attempted, using the equilibrium-state assumption, to forecast the nature of the chemical species present in the vapor and solid phase and their thermodynamic yields as a function of the CVD parameters (temperature, pressure, and inlet reactant composition). All of these studies,

however, consider only one temperature and do not address the effect on the equilibrium state of reaction by-product (e.g., HCl) addition to the reactant mixture.

The aforementioned chemistries require a deposition temperature in excess of 1000 °C to achieve acceptable rates of TiC_x deposition. In addition, the use of titanium chloride precursors leads to the formation of large quantities of HCl. These factors are detrimental to substrate materials which are thermally fragile and susceptible to corrosion as are metals and polymers. Thus, the extension of TiC_x CVD to other potentially attractive applications, particularly in the microelectronics industry, has required the development of other TiC_x CVD processes. Although, the application of plasma-assisted CVD to synthesize TiC_x has been successful, the processing temperatures are still in excess of 500 °C [105,170]. Once again, borrowing from the experience of the CVD of semiconductors, research has turned to metal-organic chemical vapor deposition (MOCVD). In this process, metal-organic precursors undergo thermolysis to yield solid deposits at a temperature below 500 °C. Several authors have explored the MOCVD route to deposit TiC_x using precursors such as tris(2,2-bipyridine) titanium (0), dichlorotitanocene, and tetraneopentyl-titanium. They have reported a deposition temperature as low as 150 °C [126,171,172]. MOCVD, however, has its disadvantages. Besides the precursors being expensive and hazardous, the fact that the carbon and titanium are tied up in one reactant molecule limits the ability to control the composition of TiC_x deposits. Furthermore, having a by-product molecule such as HCl can be a useful tool to control the reaction process, a parameter which is lost with most MOCVD chemistries.

1.2.2 Chemical Vapor Infiltration

The beginnings of CVI are traced to the manufacture of nuclear fuel elements which were produced by the consolidation of a bed of spherical particles. This process was later modified to include mixtures of particles and chopped fibers with the fuel elements [74]. Consolidation was carried out in a vertical furnace and the flow direction of the reactant gases was reversed several times to achieve uniform deposition. Matrices used included carbon, SiC, BN, W, Ni, and Al. The first use of CVI for mechanical applications was reported by Bickerdike et al. in the early 1960's [73]. Similar initial work involved the infiltration of graphite with carbon. Since then, the technique has been developed commercially such that as much as half of the carbon-carbon composites manufactured are made by CVI [30]. The use of the technique to make fiber reinforced composites was first patented by Jenkin who infiltrated alumina fiber preforms with chromium carbide [173]. After this, several authors reported the use of CVI to densify fibrous materials such as carbon, Si_3N_4 , SiC or Al_2O_3 with matrices of TiB_2 , B_4C or Al_2O_3 [48,49,53,54]. Much of the development of CVI has, however, occurred in the last two decades with most of the work concentrating at the University of Karlsruhe, the University of Bordeaux, the Society of European Propulsion (SEP), and ORNL [3,10,11,30,41,55,57-59,61-67,76,79-81,84-87]. Although the materials investigated for reinforcement and matrices are far ranging (e.g., carbon, SiC, CrC, TiC_x , B_4C , TaC, ZrC, Si_3N_4 , BN, TiB_2 , ZrO_2 , SiN_2 , and Al_2O_3), most of the recent effort has focused on the infiltration of SiC-based (Nicalon), mullite-based (Nextel) or Al_2O_3 (FP) fibrous preforms with SiC [21,31,31-35,44,79,80,89,90,174,175].

Generally, CVI processes have been classified in five categories depending on whether the preform is uniformly heated or contains temperature gradients and on how the reactant gases flow in relation to the preform. These categories are isothermal-isobaric (ICVI), thermal gradient-isobaric, isothermal-forced flow, thermal gradient-forced flow (FCVI), and pulsed CVI [30,36]. ICVI was the first developed, and is the most commonly used commercially today [30,73]. The next three categories were also used as early as the ICVI process [54,74,173]. The FCVI process, however, has been further modified at ORNL in the last decade, and can be considered a later innovation [59,76]. Radically different from the other techniques, pulsed CVI was introduced by Beatty and Kiplinger in 1970 [176]. In contrast with ICVI and FCVI, the application of pulsed CVI, however, has been limited because of the inherently long processing times, uneconomical use of precursors, and high equipment maintenance costs resulting from cyclical operation [69,177,178].

In order to find optimum conditions for infiltration and to understand the effect of the CVI process parameters, several predictive models have been proposed. As CVD transport models, these models attempt to find solutions to the equations of change for momentum, heat, and mass subject to appropriate boundary conditions. Most of these models, however, have found limited success since accurate representation of the porosity evolution as infiltration occurs is difficult. The first models published were descriptions of ICVI processes, and considered simple porosity structures (e.g., a single straight pore) and first-order reaction kinetics [55,145]. Their formulation are also based on similar approaches used in heterogeneous catalysis by Thiele and Damkohler [179,180]. Thus, the use of dimensionless numbers as the Thiele modulus is common. Although, not

applicable to real infiltration processes, these models illustrate the basic interplay between kinetic and mass transfer effects in CVI, and provide general guidance in selecting operating conditions. The major difficulty in describing the porosity evolution during infiltration of continuous fibers preforms is that the preform architecture has a multimodal porosity distribution which is invariably anisotropic. To maintain the problem tractable, several models have proposed simplified porosity structures which reflect the nearly cylindrical shape of the fibers [181-183]. In other approaches, authors have used extensions of percolation theory and Avrami's model of phase transformation to model the porosity evolution during CVI [184-190]. Yet, the failure to account for the multimodal nature of the preform porosity leads to significant discrepancies between predicted and experimentally measured densification times and composite densities. Another factor contributing to the shortcomings of these models is the use of incorrect kinetic expressions [193]. Most formulations, particularly models of SiC infiltration from methyltrichlorosilane (MTS), use first-order expressions only when multiple kinetic mechanisms may be operative in the range of CVI conditions [194]. Models of non-isothermal CVI have also been developed. In these cases, new complexities are introduced because the heat transfer properties of the developing composite vary with position as well as time. In addition, the formulation of the governing conservation equations changes as convection becomes the primary mode of reactant transport [182,192,195,196-198].

The most successful model to date is the 3-D model of forced-flow/thermal-gradient CVI published by Starr and Smith [198]. They developed a three-dimensional numerical approach using the finite volume method to discretize the preform-matrix

space. The mass and heat conservation equations include convection, diffusion, and reaction terms, while the momentum conservation equation is reduced to Darcy's law. Values for the porosity and the surface area evolution per unit volume were obtained by optical microscopy on samples of varying density. This portion of the data used in the model has been upgraded by the later use of in-situ x-ray tomographic microscopy which provides true time and position dependent evolution of these properties. The permeability is then calculated from these values. The apparent thermal conductivity at any point of the preform were related to the conductivities of the individual constituents (matrix, fiber, and porosity), resulting in logarithmic relationship with the density of the composite. This relationship was then fitted to experimental values. The model also uses a first order kinetic expression of MTS pyrolysis (perhaps its weakest point). Comparison of experimental and model predicted values of the densification times for a given back-pressure value are generally in good agreement (± 2 -3 hours). However, in some cases the discrepancies can be as large as ± 20 hours.

The mechanical properties of composites fabricated by CVI have been studied at length [14,15,44,90,199-201]. Of special interest are the properties at the matrix-fiber interface since they determine the fracture toughness of the composite [21,202-207]. In general, weak interface bonding is desirable because it leads to fiber pull-out, a mechanism responsible for crack energy absorption [23,201]. In the case of SiC-SiC composites, weak interface bonding can not be achieved without the application of an intermediate coating between the fibers and the matrix. Since vapor processing techniques are well suited for the deposition of such coatings, significant effort in the field of CVI has been devoted to the subject of interface property modification [208-210].

Coatings 0.1 to 0.3 μm thick of graphitic carbon on Nicalon fibers have been shown to promote fiber pull-out and to increase the fracture toughness of SiC-Nicalon composites [204,208,209,211]. Other coating materials such as Si_3N_4 , hexagonal BN and TiN have also been considered because of their added oxidation resistance [212-216].

1.3 Overview and Scope of the Present Work

CMCs are very promising materials which can answer new technological challenges. Nevertheless, before they can reach their full potential applicability many fabrication problems will have to be solved. In addition, the economics of these processes must be favorable for composites to replace currently used materials. Research to date has only begun to uncover “the tip of the iceberg” when considering the many possible combinations of matrix and reinforcing materials available.

In the present work the application of vapor processing techniques to fabricate TiC_x -Nicalon reinforced composites has been considered. The second chapter describes a thermodynamic approach used to predict equilibrium deposition efficiencies and compositions of TiC_x CVD from TiCl_4 , CH_4 , and H_2 precursors. In this approach, a multiphase, multispecies nonideal equilibrium algorithm was used to determine the vapor and solid phase equilibrium species and their yields as a function of temperature and inlet reactant gas composition.

The third chapter describes an experimental study of TiC_x CVD on various substrates. The experimental equipment is detailed along with characterization techniques used to analyze the TiC_x coatings. The experimental results indicate a predominant reaction-controlled mode of deposition. In addition, examination of the kinetics tends to

corroborate the mechanism reported by Hauptfear et al. [163] for TiC_x deposition from $\text{TiCl}_4\text{-C}_3\text{H}_8\text{-H}_2$ precursors. The effect of by-product poisoning was also studied. The influence of various substrates on the deposition rate and the microstructure of the coatings was also observed.

In the fourth chapter, a single pore model of FCVI is presented. The model is based on the short-contact asymptotic solution of the Graetz-Nusselt problem of heat and mass transfer. The extreme aspect ratio of the pore geometry together with the quasi-steady state assumption allows the formulation of an analytical solution. The results predict quite well general effects such as the reduction of residual porosity by enhancing the mass transfer of gaseous species while inhibiting the reaction kinetics or by the use of thermal gradients. The model also indicates that the poisoning effect of HCl coupled with the applied thermal gradient can be used to improve infiltration control of current FCVI processes.

The fifth chapter details the CVI of Nicalon preforms with TiC_x . A description of experimental procedures used for ICVI and FCVI processes is made and the results from both processes are compared. The effect of process parameters on the FCVI process is also presented. Finally, the use of HCl injection coupled with the thermal gradient used in FCVI is shown to reduce density gradients in the resulting composites.

In the sixth chapter, the process of atomic layer deposition (ALD) is investigated to deposit fiber coatings for interface property modification. Experiments involving ALD of TiC_x and TiN on flat substrates are described, and surface analysis of the resulting films is presented. The results indicate that TiO_2 is primarily deposited in both cases, and ambient contamination in the reactor chamber is believed to cause the oxide formation.

Finally, the seventh chapter provides a summary of conclusions, and outlines recommendations for future research.

CHAPTER 2 THERMODYNAMIC MODELING OF TiC_x CVD

2.1 Introduction

Fundamentally, CVD processes are the result of a complex interplay of kinetic and transport phenomena which are not only affected by processing parameters, but also the system chemistry and reactor geometry. In principle, complete model representation of a CVD process is achievable; however, the practical aspects of solving the governing equations of change can require substantial effort. Furthermore, the constitutive equations are not always well known. These complexities, therefore, lead to simpler model approaches which evolve from decoupling the various mechanistic steps involved in the deposition process. At high deposition temperatures and low gas velocity, mass transfer of reactants to the growth surface is often slow compared to the reaction kinetics at the gas-solid interface. Consequently, the overall deposition rate becomes limited by the former, and a state of chemical equilibrium is approached at the interface. Under these conditions, an equilibrium model of CVD can be used to reasonably predict certain aspects of the deposition process. Even when processing conditions do not support an equilibrium assumption, this approach is still a viable way of assessing the limits of CVD processes.

A thermodynamic approach has been used extensively in CVD research [217-219]. Typically, the information obtained from this model includes 1) the composition

of the various phases in equilibrium which can be used to determine the compatibility of the reactant chemistry with the substrate and the deposition feasibility of a given product, 2) the theoretical efficiency (product yields) of the reactant chemistry which is a factor in assessing the economics of different precursor choices, and 3) the stability ranges of the solid deposits as a function of temperature, pressure and reactant composition (CVD phase diagrams) which yield a priori information for selecting experimental process conditions. In addition, equilibrium results have been utilized for controlling dopant and impurity concentrations in semiconductor films, in identifying rate-limiting steps in the deposition process (thermochemical kinetics), and in dynamic modeling of CVD processes (e.g., CVD reactor cells) [217]. The thermodynamic equilibrium assumption, however, means that the model results are time independent. Therefore, equilibrium calculations can not reveal the true dynamic character of CVD.

Results for thermodynamic modeling of TiC_x CVD have been reported. Since most of these calculations included the variable stoichiometry of TiC_x , assessment of the Ti-C phase diagram is also reported [165-167]. The first reports were given by Vandenbulcke who computed the equilibria resulting from $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ mixtures at 1100 K and 1300 K [166,167]. His results included equilibrium compositions and yields of vapor and solid species, a CVD phase diagram containing isostoichiometric curves in the homogeneity range of TiC_x , and a comparison of phase boundaries obtained from stoichiometric and nonstoichiometric formulations of TiC_x . He also calculated specific data for the $\text{TiCl}_4\text{-CCl}_4\text{-H}_2$, $\text{TiCl}_4\text{-C}_3\text{H}_8\text{-H}_2$, and $\text{TiCl}_4\text{-C}_7\text{H}_8\text{-H}_2$ systems to compare with experimental results. Teyssandier et al. also studied the $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ system, and similarly, their results focused on the composition of the solid for comparison with

experiments [165]. The equilibria existing in the $\text{TiCl}_4\text{-CCl}_4\text{-H}_2$ system have been computed by Goto et al., who found, as did Vandenbulcke, a close correlation between the model results and experimental data [164]. They concluded that the lower stability of CCl_4 compared to CH_4 facilitates a closer approach to equilibrium, and thus better agreement between the model and experiments. Metalorganic chemistries have also been modeled. Slifirski and Teyssandier studied the dichlorotitanocene- H_2 system in order to determine conditions that minimize carbon codeposition which results from the large C/Ti ratio in the precursor molecule [169].

In this chapter, equilibrium in the Ti-C-H-Cl system produced by using $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ reactants in the range of 1300K to 1600K and 1 atm is examined. This study focuses, as others before, on the effect of temperature and reactant composition on the equilibrium compositions of the solid and gas phases. However, in contrast to previous studies, this work offers new contributions such as the addition of previously ignored sections of the CVD phase diagrams, the effects of replacing H_2 with an inert carrier gas, and the effect of HCl addition to the reactant feed on the equilibrium system. This latter aspect of the study is of particular importance since as predicted by the Le'Chatelier principle, the addition of HCl (a byproduct) should have a reversing effect on the deposition efficiency, and this effect is exploited as a means to control the deposition process of TiC_x .

2.2 Computational Methods

The problem of finding the equilibrium state of a chemical system involves the minimization of the total Gibbs energy subject to the constraints of conservation of

elemental masses, constant pressure and temperature, and nonnegativity of all the species mole numbers. The solution, thus, is a set of mole numbers which satisfy these conditions. The difficulty in finding this solution arises from the fact that while the mass balance constraints are linear in the species mole numbers, the species chemical potential functions, which describe the system total Gibbs energy, are nonlinear in the same variables. As a result, the solution procedure usually becomes iterative, and for the large systems characteristic in CVD, the use of numerical methods and digital computers is required.

Although a wide variety of computational techniques for finding equilibrium compositions have been published, most of these methods can be classified as having their origin in the methods of Brinkley [220] or White et al. [221]. Brinkley's method is the oldest one, and belongs to the category of stoichiometric or indirect techniques, which incorporate the mass balance constraints indirectly into an independent set of chemical reactions. The relationship between the elemental mass balances and the chemical reactions is then given by a linear mapping involving the mole numbers of the species, stoichiometric coefficients of the reactions, and a new set of independent variables called extents of reaction. The total Gibbs energy of the system is then minimized with respect to the new variables. The advantage of this approach is that the mass balance constraints are satisfied at the outset of the calculations and remain implicitly satisfied thereafter. Furthermore, the use of extents of reaction reduces the number of unknowns in the calculations, thus resulting in more efficient computational algorithms.

On the other hand, White's category of methods approaches the equilibrium calculations as a nonlinear optimization problem. These techniques, generally called

direct or nonstoichiometric, handle the mass balance constraints computationally by means of Lagrange multipliers, and have become the most popular class of algorithms. Nevertheless, stoichiometric techniques have computational advantages when dealing with special problems such as the case of multiphase systems involving several single-species phases. Since CVD systems are often characterized by the presence of one or more pure solid deposits, the use of stoichiometric algorithms in CVD equilibrium modeling becomes an obvious choice.

One of the most developed stoichiometric techniques is the Villars-Cruise-Smith (VCS) algorithm which uses the concept of optimized stoichiometry to maximize the computational efficiency [222]. At every step of the Gibbs energy minimization routine, the computation of the extent vector in stoichiometric algorithms requires the inversion of a Hessian matrix arising from a second order Taylor's approximation of the Gibbs energy function. This part of the calculations involves significant computational effort and is sometimes beset with singularity problems. The stoichiometric formulation of the mass balance constraints can be used to facilitate the inversion process. A consequence of expressing the mass balance constraints by means of stoichiometric equations is the division of the system species into so-called component and noncomponent species. Each noncomponent species is then viewed as the result of a reaction involving the set of component species, whose number is equal to the rank of the elemental abundance matrix and usually corresponds to the number of elements present in the system. By choosing the component species as those with the largest mole numbers, the off-diagonal elements of the Hessian matrix become negligible compared to those on the diagonal. Thus, the matrix is assumed to be diagonal which greatly simplifies the inversion process. In

conclusion, the compromise of having to select a new set of component species at various stages of iteration and not having to invert the entire Hessian matrix enhances the computational speed of the algorithm and eliminates singularity pitfalls otherwise potentially present in the inversion process.

A flowchart of this algorithm is shown in figure 2.1. At every iteration (m), the algorithm first checks for an optimum set of basis species (i.e., component species with the largest mole numbers). Otherwise, it finds a new stoichiometric matrix (N) to satisfy this requirement. N is then used with the previous iteration mole numbers to compute the diagonal elements of the Hessian matrix which, in turn, is used with the species standard chemical potentials to find the change in the extent vector ($\delta \xi$). The algorithm also calculates a step size parameter (ω) which limits the amount of change in the mole numbers vector ($n^{m+1} - n^m$) in order to achieve the greatest minimization at each iteration. After a new mole numbers vector (n^{m+1}) is computed, the Gibbs energy changes of reaction (ΔG_j) are calculated and compared to a convergence factor ($\epsilon = 10^{-7}$) to ascertain whether n^{m+1} constitutes a zero of all the ΔG_j and a potential equilibrium solution.

The program used to calculate the results presented in this chapter is a multicomponent, multiphase equilibrium algorithm based on the VCS algorithm, and first developed by Meyers [223]. A FORTRAN source code of the program, which was modified and improved for use in this study, is given in appendix 1. Modifications pertaining to the nonideal formulation of the program will be discussed in section 2.5; however, additional discussion of the program is referred to the work of Meyers.

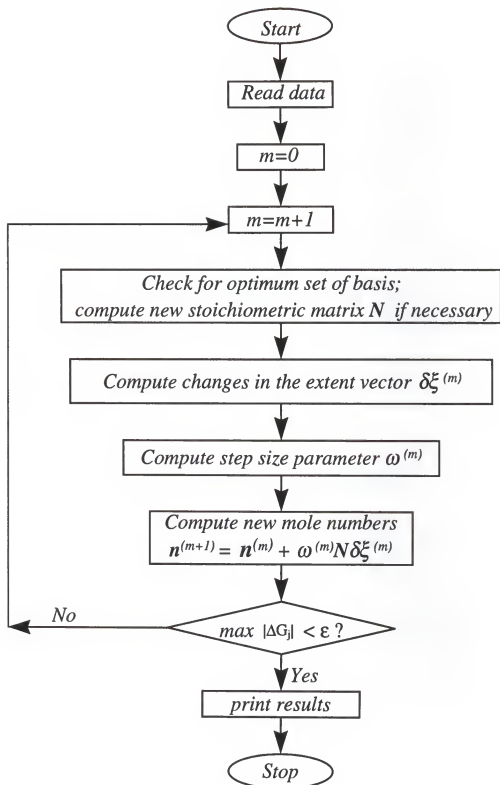


Figure 2.1 Flowchart of the VCS optimized stoichiometry algorithm [222].

2.3 The Chemical System and Thermochemical Data

As discussed by Besmann, there are two factors in equilibrium modeling which can lead to erroneous results [217]. One is the use of insufficiently accurate thermo-chemical data, while the other is the omission of species or phases whose presence can significantly alter the equilibrium state. These concerns are addressed in this section.

The chemical system used in the model was defined as a single ideal vapor phase usually in equilibrium with one or more noninteracting pure solids, or with a nonideal binary solid solution. The set of species considered in the calculations along with their thermochemical property data are listed in table 2.1. Three different databases were used as sources for the thermochemical data: Gurvich et al.[224], JANAF [225] and Barin [226]. Of these, Gurvich et al. is considered the most critical source since along with the property data, the uncertainties of these values are also given. In addition, Gurvich et al. contains the latest revisions to the data. On the other hand, JANAF is a semi-critical, semi-collective database while Barin is solely a collective database without assessment as to the data's reliability. Based on this knowledge, the data used in the equilibrium calculations, if available, originated from Gurvich et al. Failing this, the data was obtained from JANAF and lastly from Barin. However, when discrepancies in the data from Gurvich et al. and JANAF were less than 2 percent at any point in the range of 298 to 2000 K, data from JANAF were used. The reason for this choice is that several species already had heat capacity expressions fitted to data from JANAF. Data for fcc-C and fcc-Ti were obtained from lattice stability values published by Kaufman and Bernstein [227].

The chemical system was constituted to include all known species for which data were available. Since the equilibrium program used could only accommodate 50 species, preliminary calculations were made to identify vapor species whose equilibrium mole fractions were insignificant ($<10^{-12}$). The procedure was also performed with the solid species; however, the exclusion criteria was mole numbers less than 10^{-12} under all studied input conditions. The excluded vapor and pure solid species are marked by an asterisk and double asterisk respectively in table 2.1. The reduced set, thus, contained 26 vapor species, 3 pure solids (bcc-Ti, graphite, and TiC), and 2 solids in solution (fcc-Ti and fcc-C) forming the homogeneous TiC_x phase. Two different equilibrium problems were considered differing in whether the homogeneous titanium carbide phase behaves as a solid solution (TiC_x) or a stoichiometric line compound (TiC). Accordingly, fcc-Ti and fcc-C or TiC were used with the remaining species in the reduced set to define the equilibrium system. Within each of these problems four different subsets arose involving the vapor phase in equilibrium with either homogeneous titanium carbide (TiC_x or TiC), titanium carbide and graphite, titanium carbide and bcc-Ti or graphite only. In all of these cases there was a total of four components (equal to the number of elements). Thus, since in the first and last case two phases are in equilibrium, the phase rule allows for four degrees of freedom. In this study, the temperature, pressure and inlet mole fractions of CH_4 and TiCl_4 were chosen as the four independent variables. In the second and third cases as a third phase appears, the number of degrees of freedom decreases to three and only one inlet precursor mole fraction (corresponding to the additional solid phase), the temperature and pressure were used to fix the equilibrium state.

Table 2.1 Thermochemical Data of the Ti-C-H-Cl System.

Species	Ref.	$\Delta H_f^{\circ} \left(\frac{\text{KJ}}{\text{mol}} \right)$	$\Delta S_f^{\circ} \left(\frac{\text{KJ}}{\text{K mol}} \right)$	A ₀	A ₁	A ₂	A ₃	C _p [†]
H (v)	227	12.453	2.81740E-03	1.18738E-03	0	0	0	1
H ₂ (v)	227	0	0	1.67782E-03	-1.34082E-07	2.37572E-10	-4.99522E-14	2
C (v) *	227	40.939	8.69694E-03	1.19156E-03	-4.75375E-09	-2.58688E-12	3.11350E-15	2
C ₂ (v) *	226	47.439	1.06030E-02	5.88884E-03	6.07185E-07	6.32244E+00	-6.38559E-04	1
C ₃ (v) *	226	47.982	1.25895E-02	2.03107E-03	1.40311E-06	-6.46097E-10	1.07933E-13	2
CH (v) *	226	34.124	6.39543E-03	1.31958E-03	5.99405E-07	-8.13544E-11	1.62743E+01	3
CH ₂ (v)	226	22.302	3.34042E-03	1.38939E-03	1.35228E-06	-2.57787E-10	1.43042E+01	3
CH ₃ (v)	227	8.322	-4.30808E-04	-7.20296E-03	-1.94779E-07	5.68296E+01	1.55161E-03	1
CH ₄ (v)	227	-4.277	-4.61424E-03	-1.84196E-02	-9.40191E-07	1.33348E+02	3.37784E-03	1
C ₂ H (v)	226	32.476	7.59257E-03	1.90467E-03	1.29118E-06	-1.29450E-10	-3.92369E-14	2
C ₂ H ₂ (v)	227	12.952	3.35875E-03	2.58021E-03	1.66286E-06	-3.04689E-10	-4.76926E+01	3
C ₂ H ₃ (v)	226	14.852	1.44754E-03	-1.50712E-02	-9.11718E-07	7.14933E+01	2.94797E-03	1
C ₂ H ₄ (v)	227	2.997	-3.05019E-03	-2.01220E-02	-1.20348E-06	8.79986E+01	3.85136E-03	1
C ₂ H ₅ (v)	226	6.112	-5.00727E-03	-2.66142E-02	-1.56901E-06	1.45595E+02	4.93375E-03	1
C ₂ H ₆ (v)	226	-4.799	-9.95980E-03	3.08317E-04	1.01577E-05	-3.96750E-09	4.97132E-13	2
C ₃ H ₄ (diene)(v)	228	10.975	-1.97311E-03	5.65466E-04	1.12885E-05	-6.74534E-09	1.58857E-12	2
C ₃ H ₄ (yne)(v)	228	10.593	-1.73411E-03	8.39816E-04	1.06419E-05	-6.69747E-09	1.83958E-12	2
C ₃ H ₆ (cyclo)(v)	228	3.040	-9.78215E-03	2.92089E-04	1.30046E-05	4.81525E-09	4.93272E+01	3
C ₃ H ₆ (ene)(v) *	228	1.166	-8.12345E-03	2.11779E-04	1.33890E-05	-6.62251E-09	1.25841E-12	2
C ₃ H ₈ (v) *	228	-5.932	-1.54187E-02	-2.41396E-04	1.74952E-05	-9.05832E-09	1.83556E-12	2
Cl (v)	227	6.929	3.06142E-03	1.38121E-03	-9.75860E-08	-9.24713E+00	0	1
Cl ₂ (v)	227	0	0	2.10325E-03	4.97132E-08	-1.60134E+01	0	1

Table 2.1 Continued.

Species	Ref.	$\Delta H_f^\circ \left(\frac{\text{kJ}}{\text{mol}} \right)$	$\Delta S_f^\circ \left(\frac{\text{kJ}}{\text{K mol}} \right)$	A ₀	A ₁	A ₂	A ₃	C _p [†]
HCl (v)	227	-5.273	5.72299E-04	1.40296E-03	4.78011E-07	-8.19790E-11	1.18547E+01	3
CCl (v)*	226	25.110	6.12787E-03	1.03050E-03	-4.31991E-08	-9.54058E+00	1.63182E-04	1
CCl ₂ (v)*	226	12.923	2.06857E-03	2.58788E-03	8.38743E-09	-4.39967E+01	9.68922E-05	1
CCl ₃ (v)*	227	4.541	-2.48638E-03	2.38788E-03	5.63695E-06	-4.82314E-09	1.39417E-12	2
CCl ₄ (v)*	227	-5.483	-8.11668E-03	2.92976E-03	-2.40851E-07	-7.86680E+01	4.87299E-04	1
C ₂ Cl (v)*	226	30.509	6.79340E-03	-1.32789E-03	-1.70632E+00	-2.17487E+00	7.03066E-04	1
C ₂ Cl ₂ (v)*	226	11.425	2.14488E-03	2.84704E-03	3.90822E-06	-2.90774E-09	7.82457E-13	2
C ₂ Cl ₃ (v)*	226	10.870	-1.02471E-03	-7.63286E-04	-4.63059E-07	-5.37051E+01	1.02455E-03	1
C ₂ Cl ₄ (v)*	227	-0.710	-6.52462E-03	3.37070E-03	9.21200E-06	-7.45841E-09	2.08203E-12	2
C ₂ Cl ₅ (v)*	226	2.228	-9.86386E-03	5.62299E-03	-2.56064E-07	-1.35460E+02	4.82524E-04	1
C ₂ Cl ₆ (v)*	226	-8.083	-1.61142E-02	3.67366E-03	-4.88313E-07	-1.35911E+02	1.01291E-03	1
CHCl (v)*	226	17.610	2.98540E-03	2.87538E-04	2.43348E-07	-1.40281E+01	3.31709E-04	1
CHCl ₂ (v)*	226	4.221	-9.32744E-04	-2.58083E-03	-3.45394E-07	-1.52137E+01	1.02856E-03	1
CHCl ₃ (v)*	226	-5.867	-6.24620E-03	-3.94577E-03	-8.03886E-08	-3.54543E+01	1.43549E-03	1
CH ₂ Cl (v)	226	6.676	-2.56056E-04	-7.08489E-03	-4.76919E-07	3.58614E+01	1.63110E-03	1
CH ₂ Cl ₂ (v)*	227	-5.457	-5.09584E-03	1.12775E-03	7.28466E-06	-4.43881E-09	1.00519E-12	2
CH ₃ Cl (v)	227	-4.780	-4.50908E-03	7.38528E-04	6.10086E-06	-2.81644E-09	4.86090E-13	2
C ₂ HCl (v)	227	12.213	3.06381E-03	2.26300E-03	3.63289E-06	-2.06037E-09	4.29732E-13	2
C ₂ HCl ₃ (v)*	226	-1.091	-4.93989E-03	-5.11969E-03	-6.90084E-07	-4.20239E+01	1.81857E-03	1
C ₂ H ₂ Cl ₂ (v)*	226	0.195	-3.89716E-03	-9.66338E-03	-8.24976E-07	9.00476E-01	2.42665E-03	1
1,1-C ₂ H ₂ Cl ₂ (v)*	226	0.131	-4.40304E-03	-9.17641E-03	-7.90022E-07	-1.511136E+01	2.35384E-03	1
cis-C ₂ H ₂ Cl ₂ (v)*	226	0.234	-4.32228E-03	-1.00335E-02	-8.55108E-07	-1.42709E+01	2.48315E-03	1

Table 2.1 Continued.

Species	Ref.	$\Delta H_{f,298}^{\circ} \left(\frac{\text{KJ}}{\text{mol}} \right)$	$\Delta S_{f,298}^{\circ} \left(\frac{\text{KJ}}{\text{K mol}} \right)$	A ₀	A ₁	A ₂	A ₃	C _p ^o ¹
trans-C ₂ H ₂ Cl ₂ (v) *	226	0.348	-4.29520E-03	-1.01690E-02	-8.64916E-07	-3.77192E+00	2.50347E-03	1
C ₂ H ₃ Cl (v)	226	1.314	-3.14290E-03	-1.45935E-02	-9.91410E-07	2.88963E+01	3.09388E-03	1
C ₂ H ₅ Cl (v) *	228	-6.381	-9.92560E-03	-3.15483E-05	1.48782E-05	-1.05022E-08	3.16699E-12	2
Ti (v)	227	27.055	8.54216E-03	1.33402E-03	-2.88363E-07	1.61024E-10	1.19109E+01	3
TiCl (v)	227	8.819	6.10741E-03	1.79254E-04	-1.68287E-07	-1.01280E+00	3.57703E-04	1
TiCl ₂ (v)	227	-13.552	1.39952E-03	3.24257E-03	1.64065E-07	-1.02480E+01	2.01413E-05	1
TiCl ₃ (v)	227	-30.808	-2.76953E-03	2.84374E-04	-4.40710E-07	-1.24473E+01	7.28614E-04	1
TiCl ₄ (v)	227	-43.595	-6.97072E-03	2.27838E-03	-3.27548E-07	-1.20303E+01	6.01056E-04	1
He(v)	227	0	0	2.07860E-02	0	0	0	1
graphite (s)	227	0	0	-3.36998E-03	-2.74857E-07	-8.50860E+00	7.05067E-04	1
hep-Ti (s) **	227	0	0	2.62906E-03	-2.53346E-06	1.79493E-09	-5.44933E+01	3
bcc-Ti (s)	227	0.392	4.20602E-04	1.21893E-03	5.85564E-07	-3.53728E-10	1.56310E-13	2
TiH ₂ (s) **	227	-8.246	-7.52474E-03	-1.49685E-02	-1.65781E-06	2.41926E+01	2.96565E-03	1
TiCl ₂ (s) **	227	-29.446	-9.51071E-03	4.94106E-03	1.17663E-06	-2.97075E+01	-1.70328E-04	1
TiC (s)	227	-10.516	-7.00908E-04	2.93977E-03	-7.02677E-08	1.50096E-10	-8.98662E+01	3
fcc-Ti (s)	229	0.191	0	2.62906E-03	-2.53346E-06	1.79493E-09	-5.44933E+01	3
fcc-C (s)	229	7.911	8.36520E-04	-3.36998E-03	-2.74857E-07	-8.50860E+00	7.05067E-04	1

* gaseous species whose mole fractions were found to be less than 10⁻¹² after preliminary calculations.

** pure solid species whose total mole numbers were found to be less than 10⁻²⁴ after preliminary calculations.

¹ (1) $C_p^o(T) = A_0 + A_1T + A_2T^2 + A_3T^3$; (2) $C_p^o(T) = A_0 + A_1T + A_2T^2 + A_3T^3$; (3) $C_p^o(T) = A_0 + A_1T + A_2T^2 + \frac{A_3}{T^2}$; in KJ/mol.

2.4 Thermodynamic Data of the Ti-C Solid Solution

Consideration of the Ti-C solid solution in the equilibrium calculations requires a thermodynamic model to describe the chemical potentials of species (i.e., fcc-Ti and fcc-C) in nonideal solution phases. This model is generally given in the form of activity coefficients or an excess Gibbs energy expression relating the composition and temperature of the solution to the former. Several thermodynamic assessments of the Ti-C solution system have been published previously. Uhrenius used a sublattice model first proposed by Hillert and Staffansson to describe the Ti-C solution phase [228]. He calculated the model parameters by combining vapor pressure data of Ti(g) above TiC_x measured by Storms [94], the Gibbs energy of formation of stoichiometric TiC tabulated by Hultgren et al. [229], and the lattice stabilities of fcc-C and Ti given by Kaufman and Bernstein [227]. Balasubramanian and Kirkaldy, on the other hand, have proposed a model based on statistical mechanics [230]. They evaluated seven temperature dependent parameters from activity data published by Grieveson [231]. Finally, Teyssandier et al. have developed a Redlich-Kister substitutional model to describe the excess Gibbs energy of the Ti-C solution phase [232]. The eight parameters in the model were derived using activity data from Storms [94] and Koyama [233]. A comparison of the solution phase boundaries computed by the models of Teyssandier et al. and Uhrenius with the boundaries from Storm's phase diagram is shown in figure 2.2. Balasubramanian and Kirkaldy's model was not included as it was uncertain which standard states were used. From figure 2.2, the model by Teyssandier et al. has the best agreement with the phase diagram data; thus it was chosen to compute the thermodynamic properties of the solution

phase. The expression of the excess Gibbs energy of the solution phase, G_{n_i, c_i}^{ex} (KJ/g-atom), is given as

$$G_{n_i, c_i}^{ex} = x_n x_c [(a_0 + b_0 T) + (a_1 + b_1 T)(x_n - x_c) + (a_2 + b_2 T)(x_n - x_c)^2 + (a_3 + b_3 T)(x_n - x_c)^3]$$

where x_c and x_n are the mole fractions of fcc-C and fcc-Ti, respectively. The model parameter values are

$$a_0 = -716.886 \quad a_1 = -242.195 \quad a_2 = 2089.916 \quad a_3 = 1886.407 \quad \text{in KJ/g-atom}$$

$$b_0 = 0.11398 \quad b_1 = 0.04969 \quad b_2 = -0.73921 \quad b_3 = -0.99285 \quad \text{in KJ/K g-atom}$$

Since the program requires the use of activity coefficients, the following equations are applied to the excess function.

$$RT \ln(\gamma_c) = G_{n_i, c_i}^{ex} - x_n \left(\frac{\partial G_{n_i, c_i}^{ex}}{\partial x_n} \right)_{T, P}$$

$$RT \ln(\gamma_n) = G_{n_i, c_i}^{ex} + (1 - x_n) \left(\frac{\partial G_{n_i, c_i}^{ex}}{\partial x_n} \right)_{T, P}$$

where γ_c and γ_n are the activity coefficients of fcc-C and fcc-Ti, respectively.

The resulting activity coefficient expressions are

$$RT \ln(\gamma_c) = x_n^2 [\Phi - (1 - x_n) \Psi]$$

$$RT \ln(\gamma_n) = (1 - x_n)^2 [\Phi + x_n \Psi]$$

where

$$\Phi = c_0 + c_1(x_n - x_c) + c_2(x_n - x_c)^2 + c_3(x_n - x_c)^3$$

$$\Psi = 2c_1 + 4c_2(y_n - y_c) + 6c_3(y_n - y_c)^2$$

$$c_0 = a_0 + b_0 T, \quad c_1 = a_1 + b_1 T, \quad c_2 = a_2 + b_2 T, \quad c_3 = a_3 + b_3 T$$

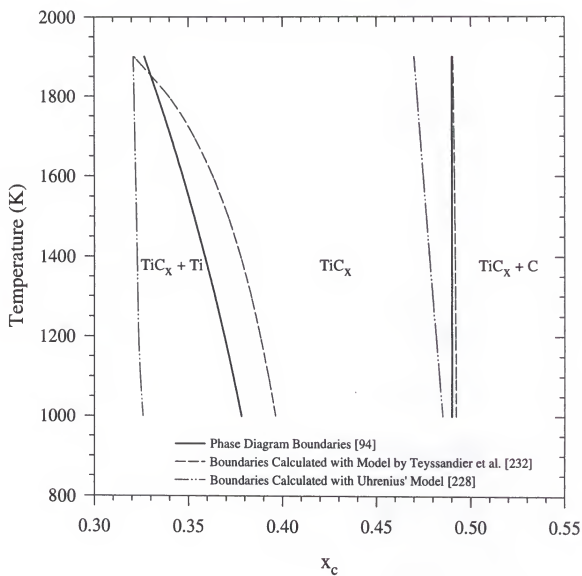


Figure 2.2 Comparison of activity coefficient models.

2.5 Nonideal Formulation of the Equilibrium program

The algorithms discussed in section 2.2 were originally designed to handle ideal systems, i.e., ideal vapor and condensed solution phases and single-species phases. The reason for this approach is that the simple structure of the chemical potential in ideal systems lends itself for the development of general, multipurpose equilibrium programs. The introduction of nonideal phases destroys this simplicity due to not only the complex functionality of the chemical potential with composition and temperature, but also the need to modify the algorithm every time a different nonideal model is used. Consequently, the problem of nonideal systems is often dealt with by superimposing additional structures to an already existing ideal system algorithm.

The program developed by Meyers uses an intermediate method to handle nonideal condensed phases [223]. The name intermediate arises from the fact that in this method the chemical potential takes on its nonideal form while the derivatives of the chemical potential retain their ideal structure. Although Meyers' program was used previously with nonideal systems, early calculations in the Ti-C-H-Cl nonideal system with this program were unsuccessful [234]. At first, this problem was attributed to the large negative deviations from ideal solution behavior in the TiC_x solution phase ($1 < \gamma_i < 10^{-15}$), but upon closer scrutiny it was found that the intermediate technique along with the iteration procedure chosen by Meyers was causing the algorithm to diverge. In Meyers' program, successive iterations use the composition of the system found in the previous iteration as an initial condition. Figure 2.3 depicts this procedure. The straight line (45° line) is the locus of initial values of the solid solution composition, while the curve denotes the computed equilibrium composition as a function of initial composition.

The intersection point (0) is, thus, the solution. A typical iteration routine is indicated by the arrows sequence. Although the first guess ($x_1=0.5649$) is close to the solution ($x_0=0.5662$), the negative slope of the equilibrium values curve repels the equilibrium result ($x_2=0.5958$) away from the solution. Accordingly, when x_2 is used as an initial condition in the next iteration, the equilibrium value ($x_3=0.0328$), represented by the intersection between the arrow and the 45° line, falls well outside the range of the graph and the stability region. Consequently, the iteration process is never convergent. This difficulty motivated the use of a different nonideal scheme and iteration procedure with Meyers' ideal routine.

A new nonideal approach, called indirect, was developed and is described below. The chemical potential of species in solution can be represented as the sum of a temperature dependent standard state chemical potential ($\mu_i^\circ(T)$), a temperature and composition dependent activity coefficient term ($RT \ln \gamma_i(T, x_i)$) and the ideal entropy term ($RT \ln x_i$).

$$\mu_i = \mu_i^\circ(T) + RT \ln \gamma_i(T, x_i) + RT \ln x_i \quad (2.1)$$

Using the initial guess of the solution composition to fix the activity coefficient results in the following pseudo-ideal form of the chemical potential of the solution species.

$$\mu_i = \mu_i^*(T, P, x_i^*) + RT \ln x_i \quad (2.2)$$

$$\text{where } \mu_i^* = \mu_i^\circ(T) + RT \ln \gamma_i(T, x_i)$$

The equilibrium computation is then performed with only the entropic term composition variable (ideal calculation), and the result compared with the initial guess. An interval halving technique is then used to select the next guess according to figure 2.3 until the

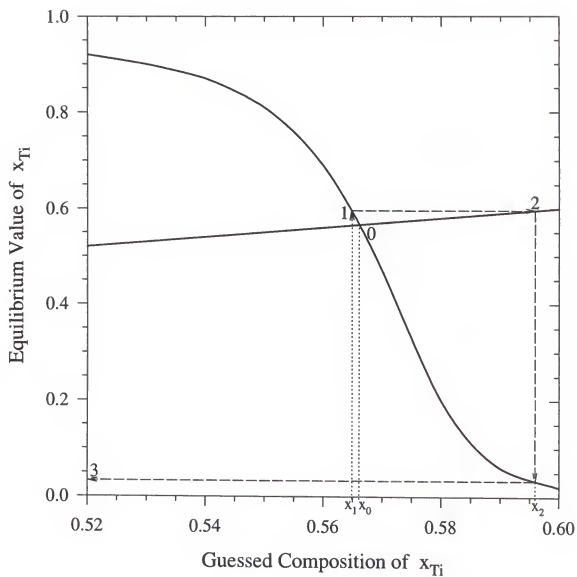


Figure 2.3 Iterative values of x_{Ti} resulting from Meyers' program.

difference between the calculated and guessed compositions differ by less than a given tolerance ($\epsilon' = 10^{-5}$). A flowchart of the modified equilibrium algorithm is shown in figure 2.4. Generally, a stoichiometric composition (i.e., $x_c = x_{Ti} = 0.5$) is used as the first guess in the routine.

2.6 Results and Discussion

2.6.1 The Vapor Phase

The effect of the precursor inlet composition on the major equilibrium vapor species at the base temperature and pressure conditions of 1500 K and 1 atm. is shown in figure 2.5. To compare the relative amounts of major and minor species, the mole fractions of all the vapor species considered are listed in table 2.2 for the case of $T=1500$ K, $P= 1$ atm. and $y_{TiCl_4}^0 = y_{CH_4}^0 = 10^{-3}$. As expected, figure 2.5 shows that the mole fractions of H_2 and H are important, and remain relatively unaffected by the input concentrations since H_2 is the carrier gas and is present in excess. The presence of significant amounts of C- or Ti-containing species is clearly determined by the ratio of $CH_4 / TiCl_4$ (R) in the inlet stream. For initial compositions with $TiCl_4$ in excess, Ti-containing species appear dominant, with their mole fractions increasing with the initial concentration of $TiCl_4$ (compare figures 2.5a,b,c and d). As the input CH_4 concentration is increased, the mole fractions of these species are unchanged, but decrease rapidly as R approaches unity. A similar behavior is observed for the C-containing species when $R > 1$ (excess CH_4). As will be discussed in section 2.6.2, an input concentration with one of the precursor in excess is also associated with the codeposition of the corresponding excess pure solid element with TiC_x . This is also evidenced by the fact that the activities of $C(s)$

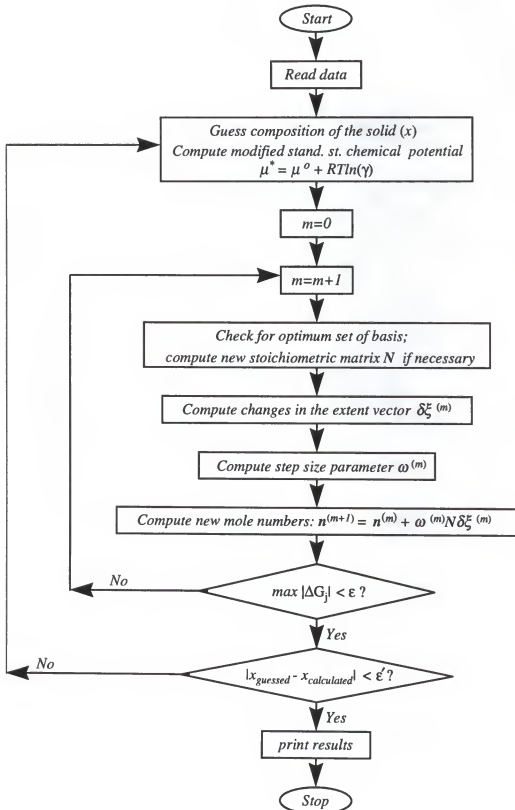


Figure 2.4 Optimized stoichiometric algorithm with indirect nonideal scheme.

Table 2.2 Equilibrium Mole Fractions of All Vapor Phase Species Considered at 1500 K, 1 atm. and $y_{\text{TiCl}_4}^0 = y_{\text{CH}_4}^0 = 10^{-3}$.

Species	Equilibrium Mole Fraction	Species	Equilibrium Mole Fraction
H (v)	1.75E-05	C ₃ H ₆ (cyclo)(v)	1.31E-13
H ₂ (v)	9.96E-01	Cl (v)	5.64E-08
CH ₂ (v)	6.81E-13	Cl ₂ (v)	9.47E-13
CH ₃ (v)	5.01E-08	HCl (v)	3.99E-03
CH ₄ (v)	1.17E-04	CH ₂ Cl (v)	9.50E-13
C ₂ H (v)	3.26E-16	CH ₃ Cl (v)	4.49E-10
C ₂ H ₂ (v)	2.42E-08	C ₂ HCl (v)	5.84E-14
C ₂ H ₃ (v)	7.77E-12	C ₂ H ₃ Cl (v)	1.07E-13
C ₂ H ₄ (v)	6.05E-09	Ti (v)	2.18E-14
C ₂ H ₅ (v)	5.49E-13	TiCl (v)	1.69E-11
C ₂ H ₆ (v)	5.29E-11	TiCl ₂ (v)	3.93E-08
C ₃ H ₄ (diene)(v)	6.31E-14	TiCl ₃ (v)	2.34E-07
C ₃ H ₄ (yne)(v)	1.77E-13	TiCl ₄ (v)	3.03E-09

and Ti(s) (also plotted on figures 2.5a-d) become unity in the same range of input reactant concentrations. The symmetrical decrease in both groups of vapor species about $R=1$ identifies the range of conditions favoring TiC_x formation, as the available C and Ti in the vapor combine to form TiC_x . Once again, the C(s) and Ti(s) activities are seen to change rapidly in this region, confirming the formation of TiC_x . These observations are in qualitative agreement with the work of Vandenbulcke at 1300 K [166], yet his results deviate toward lower CH_4 and TiCl_4 inlet concentrations compared to the results in this study.

For $R \ll 1$ and $y_{\text{TiCl}_4}^0 = 10^{-3}$, the predominant titanium chloride species is TiCl_2 , but the calculation at $y_{\text{TiCl}_4}^0 = 10^{-2}$ indicates that TiCl_3 is the primary species. In this region of $R \ll 1$, essentially all the carbon is found in TiC_x , and the Ti(s) and C(s) activities are fixed by the two phase Ti(s) and $\text{TiC}_x(\text{s})$ mixture. Increasing $y_{\text{TiCl}_4}^0$ under these conditions drives the disproportionation of TiCl_4 into TiCl_3 and TiCl_2 . As the value of R approaches unity only a single phase TiC_x solid solution exists and both component activities are variable. The Ti/Cl ratio in the vapor phase decreases as more carbon becomes available, and the driving force for disproportionation decreases causing TiCl_4 to become the dominant Ti vapor species. This competition between C and Cl for Ti in the vapor phase produces an equilibrium mole fraction of TiC_4 that increases as R approaches unity, and then sharply decreases for $R > 1$. Because of the stability of the C-H bond (413 KJ/mol) relative to the C-C bond (347 KJ/mol), the precursor CH_4 molecule is also the predominant hydrocarbon species at equilibrium. At higher CH_4 input concentrations unsaturated hydrocarbon species (C_2H_2 and C_2H_4), stabilized by triple and double bonds, begin to appear.

The equilibrium mole fraction of HCl is primarily determined by the input TiCl_4 mole fraction since H_2 is in excess, and TiCl_4 the only chlorine atom source. A slight variation in the equilibrium HCl mole fraction is observed in the vicinity of $R=1$. This slight variation is associated with the different solid deposition domains that result from varying the precursor composition. For R values less than one, only a small fraction of the excess TiCl_4 is used to form TiC_x . Additional TiCl_4 is consumed in the codeposition of pure Ti , but the majority of Ti remains in the vapor phase as TiCl_x reducing the equilibrium HCl concentration. As R approaches unity, the pure Ti(s) phase disappears.

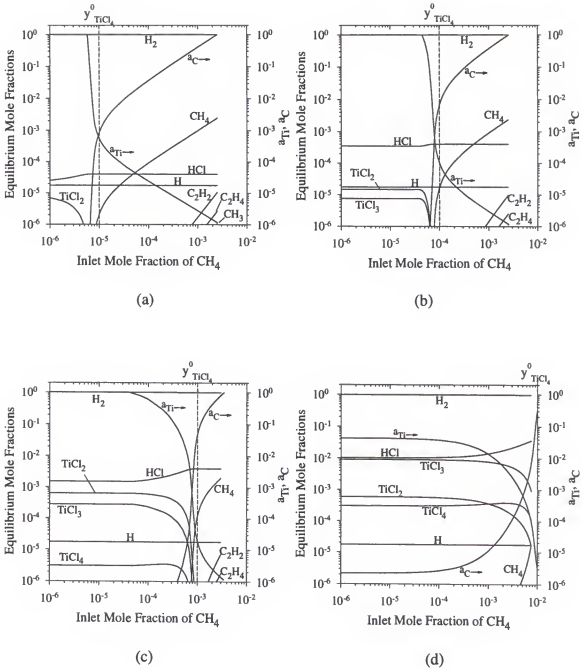


Figure 2.5 Effect of the inlet CH_4 and TiCl_4 mole fractions on the equilibrium vapor phase composition ($T=1500\text{ K}$ and $P=1\text{ atm}$).

a) $y^0_{\text{TiCl}_4}=10^{-5}$, b) $y^0_{\text{TiCl}_4}=10^{-4}$, c) $y^0_{\text{TiCl}_4}=10^{-3}$, d) $y^0_{\text{TiCl}_4}=10^{-2}$.

The Ti(s) activity decreases and the C(s) activity increases, thus resulting in the formation of more TiC_x . The accompanying additional release of Cl while TiC_x forms increases the equilibrium mole fraction of HCl. Ultimately, for values of R much greater than one, most of the Cl is released as the majority of Ti appears in TiC_x , and a maximum concentration of HCl is calculated. Further increases in R lead to C codeposition, and thus, the HCl concentration remains constant.

Figure 2.6 shows the equilibrium vapor phase composition as a function of the inlet composition at four different temperatures and $y_{\text{TiCl}_4}^0 = 10^{-4}$. As the temperature increases the disproportionation of TiCl_4 is favored due to entropic effects. Consequently, the equilibrium concentration of HCl increases with temperature and the slight variation of y_{HCl}^0 at low and high R values diminishes. As the temperature increases, entropic considerations again increase the mole fractions of other hydrocarbon species. Less stable species such as, C_2H_4 are dominant at the lower temperature; however, at higher temperatures, CH_4 decomposition favors the formation of more stable species such as C_2H_2 and CH_3 .

In several studies [55,62,166,167,169], the equilibrium of the Ti-C-H-Cl system has been computed assuming that TiC_x behaves only as a stoichiometric compound ($x=1$). The thermodynamic properties of TiC are obtained by extrapolating the properties of TiC_x , at the boundary between the TiC_x and $\text{TiC}_x + \text{C}$ regions, to a value of $x=1$. In this study, the stoichiometric case was also considered in order to evaluate the validity of this approximation. Figure 2.7 shows a comparison of the vapor phase equilibria resulting from the stoichiometric (TiC) and the nonstoichiometric (TiC_x) cases at various temperatures and input precursor concentrations. It is evident that for R values that lead to

codeposition of C or Ti, both formulations give the same results for the major vapor species. Under these conditions one of the solid elemental activities is fixed by the codeposition. (e.g., for $R \ll 1$, $a_{Ti} = 1$ when Ti and TiC are codeposited), and the equilibrium vapor phase contains no species of the other element (e.g., carbon species for $R \ll 1$). Consequently, the overall equilibrium becomes dominated by the equilibrium of the subsystem including the solid and vapor species of the excess element. Therefore, for values of R departing sufficiently from unity, there is not a difference between the vapor phase equilibrium resulting from either TiC or TiC_x . However, for R near unity, where pure TiC_x is obtained, the stoichiometric formulation tends to overestimate the equilibrium concentrations of the titanium chlorides and underestimate those of HCl and the hydrocarbon species. These discrepancies also increase with higher temperatures. The differences in the equilibrium mole fractions are evidently the result of the higher C content of TiC relative to TiC_x throughout the homogeneity range. This causes the consumption of greater quantities of carbon from the vapor phase thus reducing the equilibrium mole fractions of these species. On the other hand, since x is greater in TiC than in TiC_x , the activity of Ti(s) becomes unity for the stoichiometric case at R values closer to unity. Therefore, the equilibrium mole fractions of Ti vapor species are larger in the stoichiometric case for $R < 1$ and $a_{Ti} < 1$.

2.6.2 The Solid Phase

One of the primary concerns in thermodynamic modeling is the prediction of initial condition ranges which yield desired solid phases. TiC_x is a single homogeneous phase of variable stoichiometry (a solid solution with limited miscibility). As the C

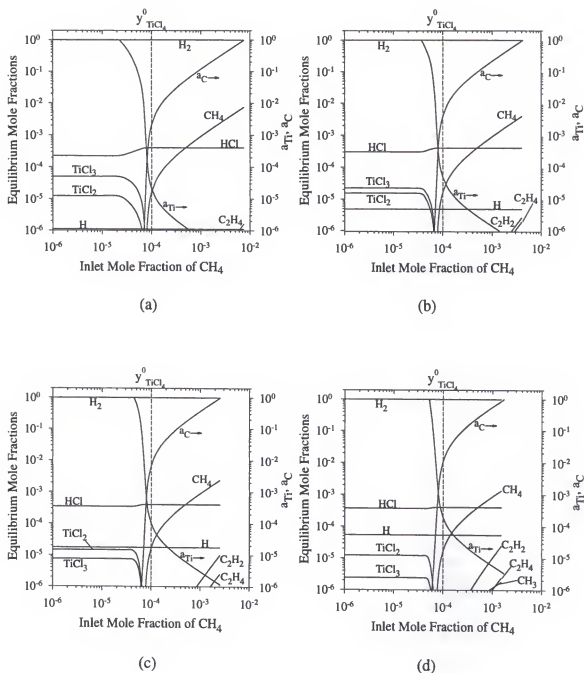


Figure 2.6 Effect of inlet CH_4 mole fraction and temperature on the equilibrium vapor phase composition ($P = 1 \text{ atm}$, $y^0_{\text{TiCl}_4} = 10^{-4}$).

a) $T = 1300 \text{ K}$; b) $T = 1400 \text{ K}$; c) $T = 1500 \text{ K}$; d) $T = 1600 \text{ K}$.

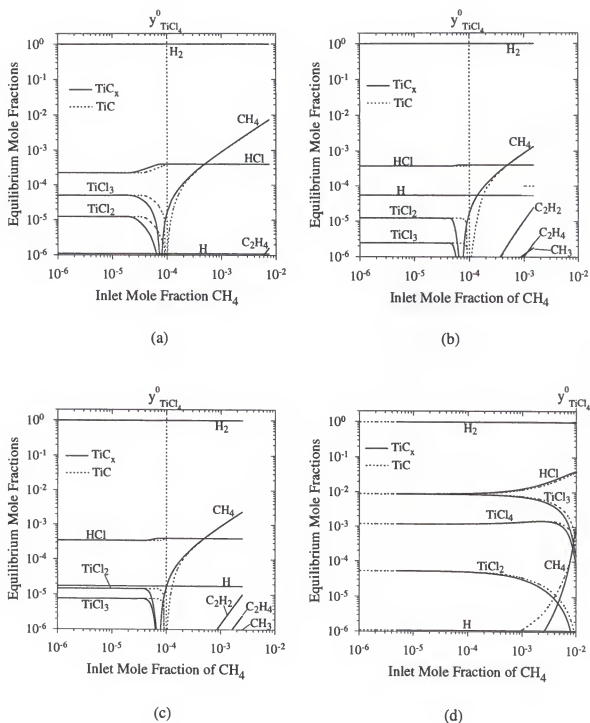


Figure 2.7 Comparison of the vapor phase equilibria resulting from considering stoichiometric or non-stoichiometric TiC in the equilibrium system ($P=1\text{ atm}$).
 a) $T=1300\text{ K}$, $y_{\text{TiCl}_4}^0=10^{-4}$; b) $T=1600\text{ K}$, $y_{\text{TiCl}_4}^0=10^{-4}$; c) $T=1500\text{ K}$, $y_{\text{TiCl}_4}^0=10^{-4}$; d) $T=1500\text{ K}$, $y_{\text{TiCl}_4}^0=10^{-2}$.

activity increases, TiC_x becomes saturated and a two phase region develops where TiC_x appears in equilibrium with graphite. On the other hand, for increasing Ti activities TiC_x saturates with Ti and is found in equilibrium with hcp-Ti below 1193 K and with bcc-Ti in the range of 1193 K to 1925 K. Figure 2.8 shows calculated CVD phase diagrams which indicate the solid phases deposited as a function of precursor composition at two different temperatures and $P = 1$ atm. Since the temperature is above 1200 K, solid Ti is in bcc form. For comparison, the solid phase fields that result when stoichiometric TiC is considered as a line compound are also shown. Surprisingly, besides the expected solid domains (i.e., TiC, $\text{TiC}+\text{C}$ and $\text{TiC}+\text{Ti}$), a domain was found at high $y_{\text{TiCl}_4}^0$ where solely graphite is deposited.

As shown in figure 2.8, three features of the TiC_x domain boundary with the TiC_x+C and C domains can be observed. At dilute TiCl_4 reactant inlet mole fractions the boundary between the single phase TiC_x and the two- phase TiC_x+C regions is independent of $y_{\text{TiCl}_4}^0$. The location of this dilute region boundary, as indicated in the figure, is nearly proportional to the CH_4 inlet mole fraction and matches the graphite deposition boundary in the C-H equilibrium system. This is an expected result since CH_4 is in excess, and thus, along with H_2 dominates the overall equilibrium. In the middle to upper range of TiCl_4 inlet mole fractions, the boundary shifts toward higher $y_{\text{CH}_4}^0$ in a nearly linear fashion, consistent with retaining the values of R close to unity. Thus, this is the region of most efficient reactant utilization. Finally, when the TiCl_4 inlet mole fraction becomes comparable to the carrier gas (H_2) mole fraction, the boundary shifts back toward lower $y_{\text{CH}_4}^0$, and becomes insensitive to this precursor. This feature,

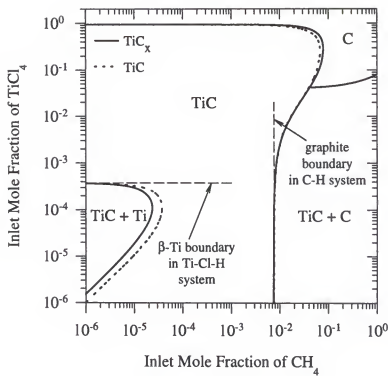
coincidentally, occurs in the section of the boundary which separates TiC_x from pure graphite deposition. In this region of $y_{\text{TiCl}_4}^0$, there is not enough H_2 to facilitate the reduction of TiCl_4 to form TiC_x . Consequently, the disproportionation of TiCl_4 to Ti-subchlorides becomes the dominant reaction involving TiCl_4 , and at equilibrium, most of the available Ti remains in stable TiCl_x species. Since less Ti is available to form TiC , only graphite is deposited. However, in this case, the deposition of graphite is observed to occur at inlet CH_4 mole fractions below the C-H system graphite deposition boundary. This is the result of the formation of Cl-containing hydrocarbon species such as CH_3Cl and CH_2Cl which become important in the absence of H_2 to compete for the Cl released by the disproportionation of TiCl_4 . These species, in turn, are less stable than hydrocarbon radicals (e.g., CH_3 and CH_2), and yield graphite more readily at relatively lower inlet mole fractions of CH_4 .

Similar features are also observed, in the domain boundary between TiC_x and $\text{TiC}_x + \text{Ti}$. At low inlet mole fractions of both precursors, the boundary changes, once again, in a linear fashion as R remains near unity. For excess concentrations of TiCl_4 , the boundary, as expected, becomes insensitive to $y_{\text{CH}_4}^0$, and matches the Ti-Cl-H system Ti deposition boundary. Similarly to the graphite case, with TiCl_4 in excess, the deposition of Ti becomes the dominant feature of the overall equilibrium, and the boundary changes nearly proportionally to $y_{\text{TiCl}_4}^0$.

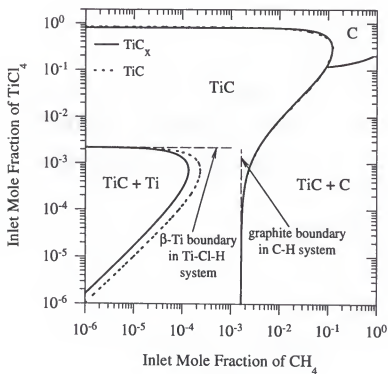
The $\text{TiC}_x/\text{TiC}_x + \text{C}$ boundary locations calculated when considering instead the line compound TiC are in close agreement with those calculated for the solid solution TiC_x . The extent of the $\text{TiC} + \text{Ti}$ two-phase field, however, is clearly larger in the stoichiometric case. This large difference can be attributed to the fact that stoichiometric

sum of Ti and C chemical potentials in TiC_x (i.e., $\mu_{\text{Ti}} + x \cdot \mu_{\text{C}}$) is less than the Gibbs energy of formation of the hypothetical line compound TiC . The lower carbon chemical potential requires less inlet CH_4 at a fixed $y_{\text{TiCl}_4}^0$, or more TiCl_4 at a fixed $y_{\text{CH}_4}^0$ to saturate TiC_x with Ti. At higher temperatures, the solid solution range of TiC_x decreases as the volatilities of C and Ti in TiC_x increase (see figure 2.9). TiC_x sublimes congruently; thus, a reduction in the deposition domain range on both sides is expected. The only exception to this trend is a small region at high input concentrations of both CH_4 and TiCl_4 . In this region, although conditions favor the disproportionation of TiCl_4 , the higher temperatures lead to the break down of Ti-subchlorides making available more Ti from the vapor phase to form TiC_x . Once again these results are in agreement with those of Vandenbulcke at 1300 K and compare well with the work of Teyssandier et al. at 1800 K [165,166].

Clearly, thermodynamic calculations neglecting the limited extent of solid solution of TiC_x can not only lead to errors in the prediction of the solid domain boundaries, but more trivially, yield no information as to the real composition of TiC_x in the homogeneous region. Modeling the TiC_x as a nonideal solid solution shows a sensitivity of the deposited composition on the inlet precursor composition and to a lesser extent on the growth temperature (figures 2.10 to 2.13). As calculated previously (figure 2.9), for increasing temperature, the single phase TiC_x domain becomes slightly narrower. Consistent with the phase diagram, the composition of TiC_x along the C-rich solidus is almost constant ($x=0.97$) in the temperature range studied. On the other hand, the Ti-rich solidus shows a C decrease with increasing temperature.



(a)



(b)

Figure 2.8 Comparison of solid phase boundaries that result for stoichiometric and non-stoichiometric TiC ($P = 1 \text{ atm}$).

a) $T = 1300 \text{ K}$; b) $T = 1600 \text{ K}$.

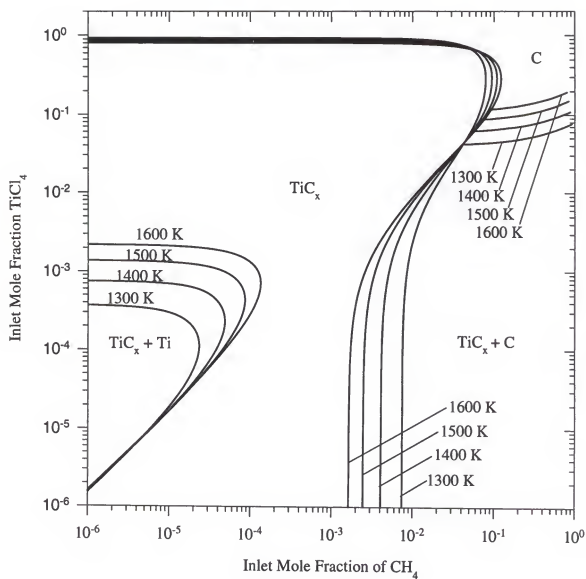


Figure 2.9 Variation of the solid phase boundaries with temperature and inlet mole fractions of CH₄ and TiCl₄.

The variation of the isostoichiometric curves with the inlet precursor mole fraction can be explained with the same arguments used to describe similar changes in the domain boundaries. In cases when $y_{\text{CH}_4}^0$ is in excess, a given composition of TiC_x remains insensitive to $y_{\text{TiCl}_4}^0$, and changes slightly with $y_{\text{CH}_4}^0$ as $y_{\text{TiCl}_4}^0$ increases. This is the result of the unavailability of TiCl_4 ; thus, $y_{\text{TiCl}_4}^0$ has to change orders of magnitude before any significant change in the position of the curve occurs. The opposite also holds on the other side of the 45° line; i.e., when $y_{\text{TiCl}_4}^0$ is in excess. The largest changes in the isostoichiometric domains, once again, occur when R is near unity and the reactants are in optimum proportion for reaction. Peculiarly, as $y_{\text{TiCl}_4}^0$ increases from this linear region to higher concentrations of TiCl_4 , double values of TiC_x composition are obtained. The value at the higher $y_{\text{TiCl}_4}^0$ is the result of less Ti becoming available for solid formation because of the disproportionation of TiCl_4 . Thus, although $y_{\text{TiCl}_4}^0$ is in excess, it yields the same TiC_x composition as a lower $y_{\text{TiCl}_4}^0$ in proportion to $y_{\text{CH}_4}^0$. This explains why the curves bend back toward lower $y_{\text{CH}_4}^0$ as $y_{\text{TiCl}_4}^0$ increases, and why the linear portion of the isostoichiometric curves does not extend to $y_{\text{CH}_4}^0 = y_{\text{TiCl}_4}^0 \equiv 1$.

The variation of the C/Ti ratio (x) in TiC_x with the reactant input mole fractions and temperature is shown in figures 2.14 to 2.17. At high inlet mole fractions of TiCl_4 , x remains above the limiting value at the $\text{TiC}_x + \text{Ti}$ boundary even for the lowest CH_4 input concentrations. This corresponds to the region above the $\text{TiC}_x + \text{Ti}$ domain in the CVD diagram where no Ti codeposits even though the CH_4 concentration is orders of magnitude lower than that of TiCl_4 . As the CH_4 mole fraction is increased in these cases, x remains fairly constant throughout the domain, before rapidly reaching the value of 0.97

at the $\text{TiC}_x + \text{C}$ boundary. For TiCl_4 concentrations that cross the $\text{TiC}_x + \text{Ti}$ domain the opposite is observed. As the CH_4 mole fraction increases, x rises rapidly at first, and then changes more gradually toward 0.97. The variation of x from one domain boundary to the other occurs even faster at higher temperatures. This is expected since the homogeneous TiC_x domain becomes narrower in the inlet precursor mole fractions range at higher temperatures. In figures 2.18a and b, the sensitivity of x with the CH_4 inlet mole fraction ($dx/dy_{\text{CH}_4}^0$) is plotted as a function of the CH_4 inlet mole fraction for various TiCl_4 inlet mole fractions and two temperatures. From these plots, it is evident that the magnitude of the rate of change of x depends on the ratio of the precursor inlet mole fractions (R). When R departs from unity, the changes in x as the mole fraction of CH_4 increases are relatively small. In figures 2.10 to 2.13, this is the case for TiCl_4 concentrations which do not cross the $\text{TiC}_x + \text{Ti}$ domain since for most of the TiC_x domain, TiCl_4 remains in excess. For lower TiCl_4 concentrations, $dx/dy_{\text{CH}_4}^0$ remains low while TiCl_4 is in excess, reaches a maximum near $R=1$, and decreases as CH_4 appears in excess. Therefore, the fastest changes in the solid composition (x) occur by increasing or decreasing the precursor composition while keeping their ratio (R) near unity.

2.6.3 Effect of HCl Injection and Using an Inert as Carrier Gas

HCl is a byproduct of the overall reaction that yields TiC_x . Consequently, Le'Chatelier's principle suggests that HCl addition to the reactant feed would oppose the equilibrium formation of TiC_x . This effect can be used to control the deposition yield of TiC_x and possibly its composition. To determine the expected effect of adjusting the inlet

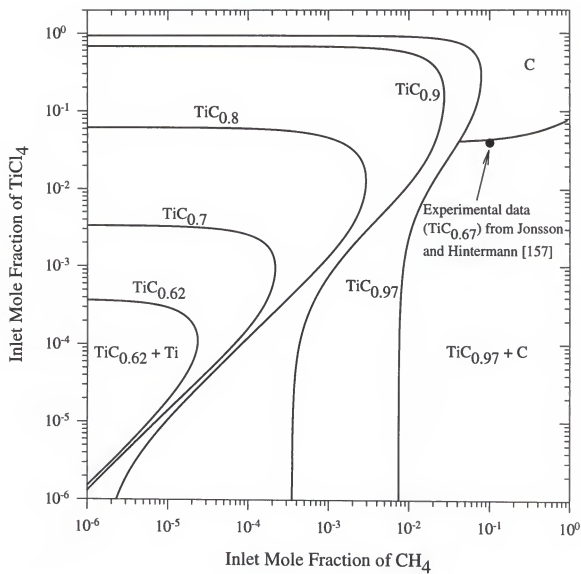


Figure 2.10 Isostoichiometric curves in the homogeneous region of TiC_x ($T=1300\text{ K}$).

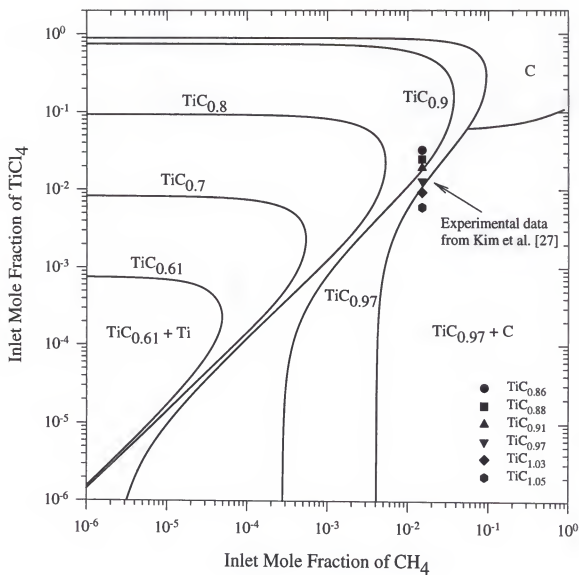


Figure 2.11 Isostoichiometric curves in the homogeneous region of TiC_x ($T=1400\text{ K}$).

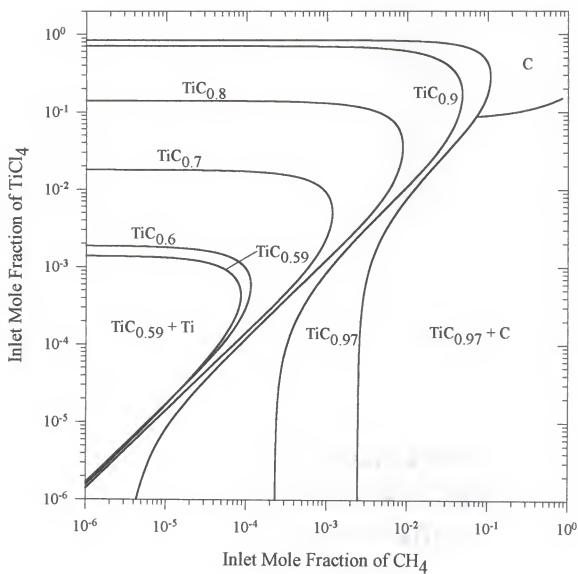


Figure 2.12 Isostoichiometric curves in the homogeneous region of TiC_x ($T=1500\text{ K}$).

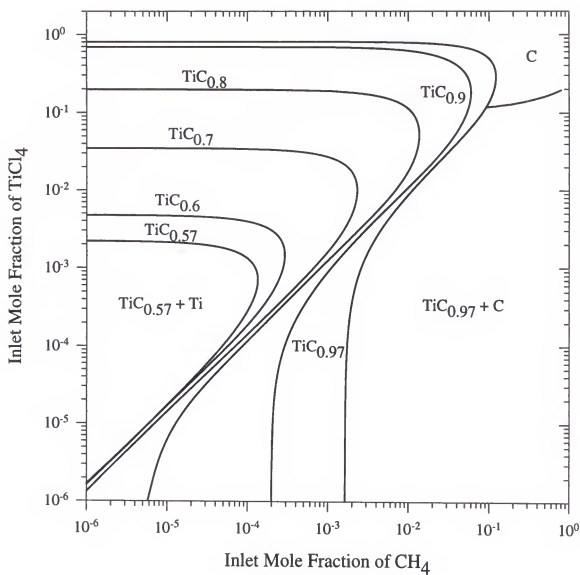


Figure 2.13 Isostoichiometric curves in the homogeneous region of TiC_x ($T=1600\text{ K}$).

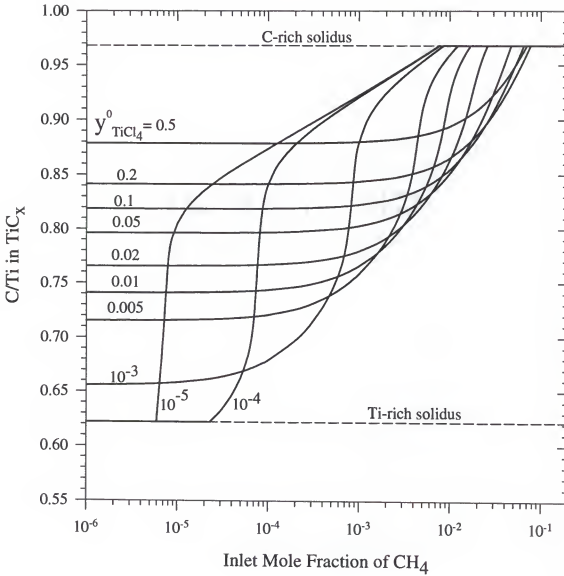


Figure 2.14 Variation of the composition of TiC_x with the inlet mole fractions of CH_4 and $TiCl_4$ ($T = 1300$ K).

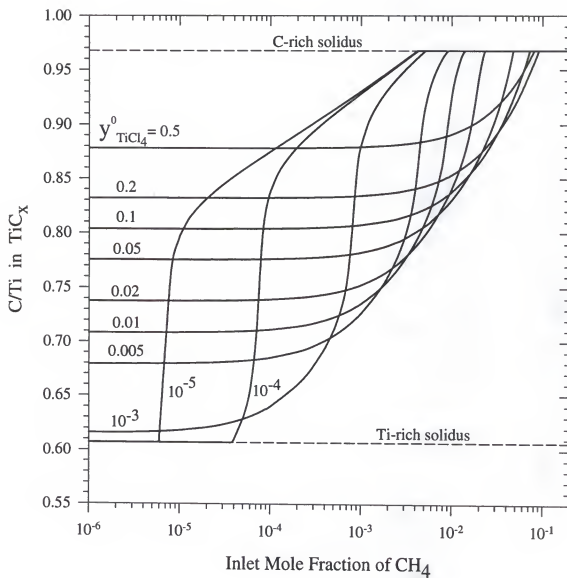


Figure 2.15 Variation of the composition of TiC_x with the inlet mole fractions of CH_4 and $TiCl_4$ ($T = 1400$ K).

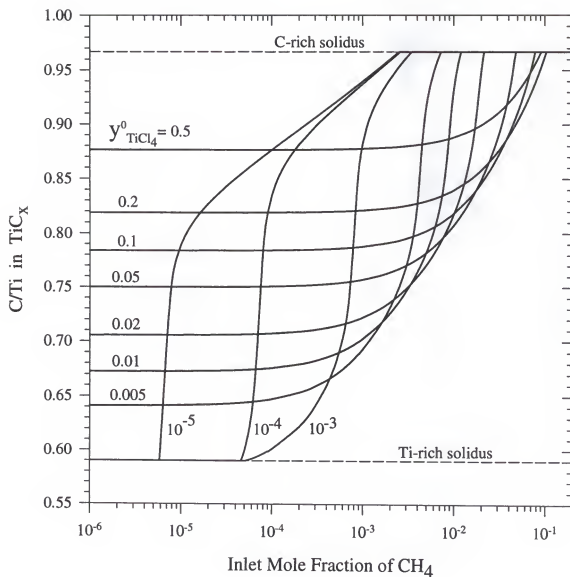


Figure 2.16 Variation of the composition of TiC_x with the inlet mole fractions of CH_4 and TiCl_4 ($T = 1500 \text{ K}$).

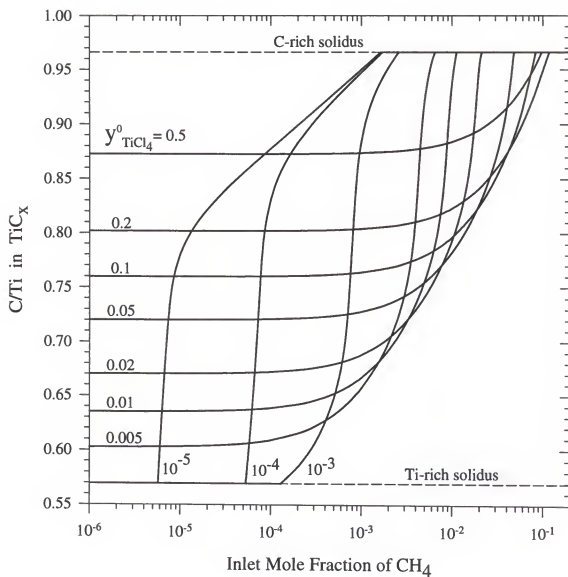


Figure 2.17 Variation of the composition of TiC_x with the inlet mole fractions of CH_4 and $TiCl_4$ ($T = 1600$ K).

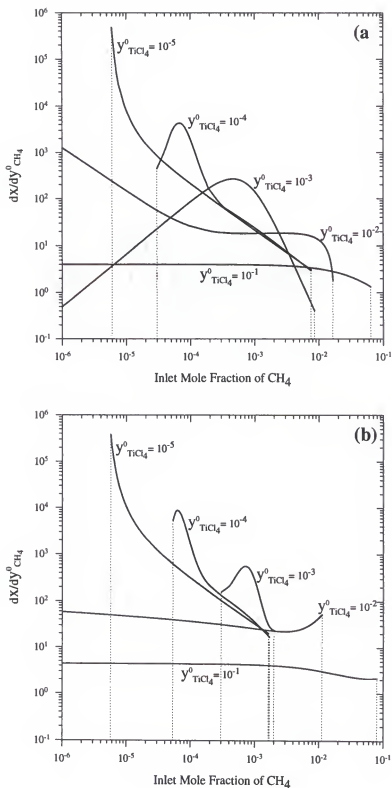


Figure 2.18 Sensitivity of the TiC_x solid composition on the CH_4 inlet mole fraction as a function of the inlet mole fractions of CH_4 and TiCl_4 .
a) $T=1300\text{ K}$; b) $T=1600\text{ K}$.

HCl mole fractions as well as replacing the carrier gas with an inert species, chemical equilibrium calculations were performed as described in this section.

The influence of HCl injection on the vapor phase equilibrium is shown in figure 2.19 with $y_{\text{CH}_4}^0 = 10^{-3}$ and $y_{\text{TiCl}_4}^0 = 10^{-4}$. Under these conditions, single phase TiC_x is the only condensed equilibrium phase. While the hydrocarbon species are practically unaffected by the addition of HCl, the equilibrium mole fractions of Cl-containing species steadily rises as the inlet mole fraction of HCl is increased above the level present with no HCl addition ($y_{\text{HCl}}^0 \approx 10^{-3}$). The first order effect of increasing the Cl atom content of the vapor phase is to increase the HCl fraction of the vapor. This is true since most of the vapor phase is H_2 , and thus, its fugacity is fixed. Consequently, an increase in the Cl atom content will cause a nearly linear increase y_{HCl}^0 above the threshold value. The mole fractions of the TiCl_x species increase in a similar fashion with their relative amounts depending on the temperature. Higher temperature favors the formation of TiCl_x species with the lowest x due to entropic considerations.

The effect of adding HCl on the equilibrium yield of single phase TiC_x is presented in figure 2.20. The equilibrium yield was defined as the ratio of the equilibrium mole numbers of TiC_x to the equilibrium mole numbers of the limiting reactant (TiCl_4 or CH_4). As expected, HCl injection shifts the overall equilibrium yield of TiC_x toward lower values. At these conditions, the etching effectiveness of HCl is somewhat diminished at higher temperatures (see figure 2.21). The intersection of the equilibrium yield surface in figure 2.21 with the temperature-HCl mole fraction plane results then in the curve shown in figure 2.22. This curve represents a boundary between conditions which yield TiC_x deposition and TiC_x etching. Qualitatively, the deposition zone lies at

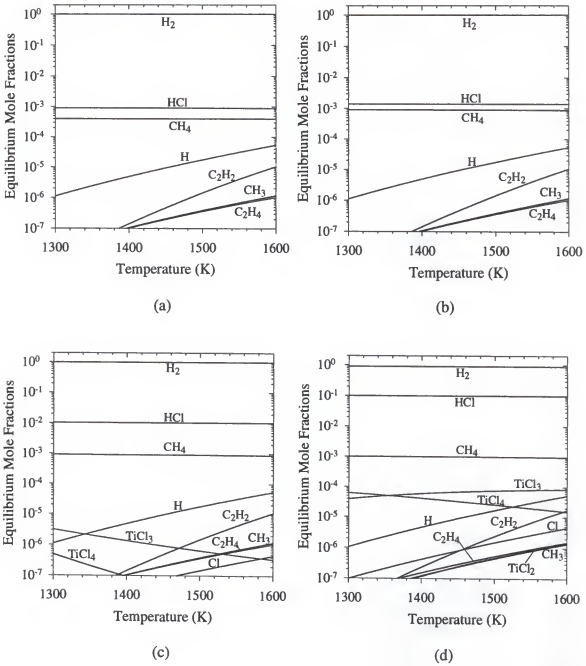


Figure 2.19 Effect of HCl injection on the equilibrium vapor phase composition ($y_{CH_4}^0 = 10^{-3}$, $y_{TiCl_4}^0 = 10^{-4}$).

a) $y_{HCl}^0 = 0$; b) $y_{HCl}^0 = 10^{-3}$; c) $y_{HCl}^0 = 10^{-2}$; d) $y_{HCl}^0 = 10^{-1}$.

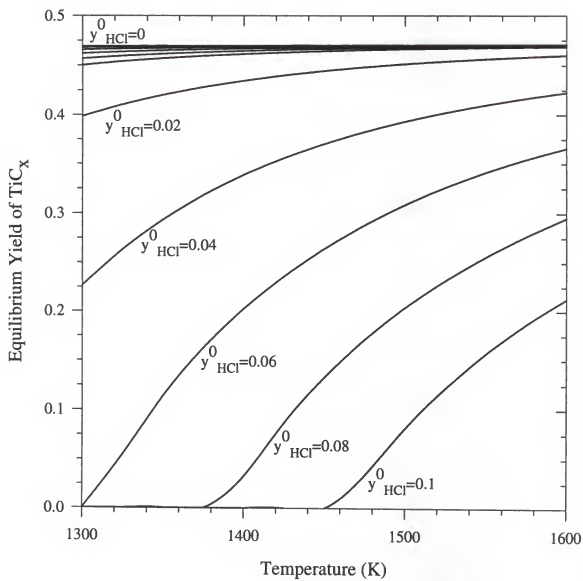


Figure 2.20 Effect of HCl injection on the equilibrium yield of TiC_x
 $(y_{\text{CH}_4}^0 = 10^{-3}, y_{\text{TiCl}_4}^0 = 10^{-3})$.

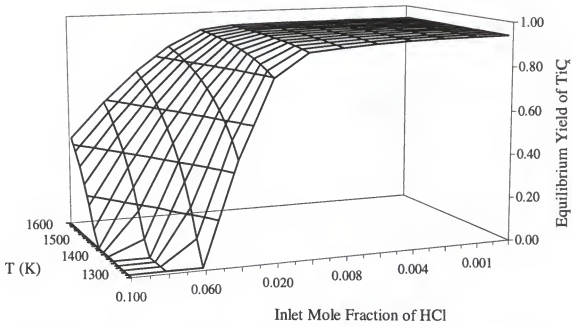


Figure 2.21 Variation of the equilibrium yield of TiC_x with temperature and HCl inlet concentration ($y_{\text{CH}_4}^0 = 10^{-3}$, $y_{\text{TiCl}_4}^0 = 10^{-3}$).

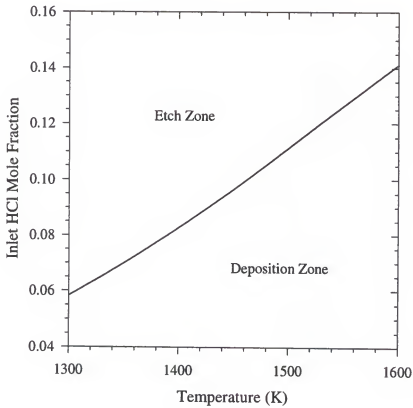
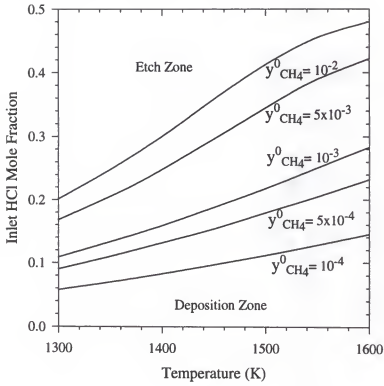
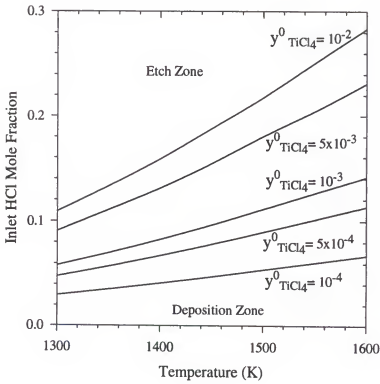


Figure 2.22 Etch-deposition zones of TiC_x as a function of the deposition temperature and inlet HCl concentration ($y_{\text{CH}_4}^0 = 10^{-3}$, $y_{\text{TiCl}_4}^0 = 10^{-3}$).



(a)



(b)

Figure 2.23 Effect of precursor composition on the TiC_x etch-deposition boundary.
 a) $y_{\text{TiCl}_4}^0 = 10^{-2}$; b) $y_{\text{CH}_4}^0 = 10^{-3}$.

low inlet concentrations of HCl and high temperatures. The variation of the etch-deposition boundary with reactant mole fraction is shown in figure 2.23. Predictably, the etch-deposition boundary shifts toward higher inlet concentrations of HCl as the reactant mole fractions are increased since the driving force for deposition increases and more chlorine is necessary to etch an equivalent amount of TiC_x . For this reason also the sensitivity of the boundary with temperature increases as the reactant concentrations increase.

The effect of adding HCl on the equilibrium composition of single phase TiC_x is shown in figure 2.24. For a given temperature, x increases as the inlet mole fraction of HCl increases, indicating preferential etching of Ti. This discrimination occurs because Ti is more readily transferred from the solid to the vapor phase through the formation of stable TiCl_x species, while Cl-containing carbon and hydrocarbon species have much lower stability. The variation in TiC_x composition with temperature at a given HCl inlet mole fraction is less important which suggests that the deposition of TiC_x under a temperature gradient would result in a fairly constant solid composition.

Figure 2.25a and b show the effect on the CVD diagram of gradually replacing H_2 with He as the carrier gas at 1300 K and 1600 K. As the inlet ratio of He to H_2 (α) increases, the C domain increases relative to all the other domains. At 1300 K and $\alpha=100$, and 1600 K and $\alpha=10^4$, the $\text{TiC}_x + \text{Ti}$ domain disappears in the range of precursor inlet mole fractions considered. Replacing H_2 completely with He ($\alpha = \infty$), results in the deposition of only C at all precursor inlet mole fractions and temperatures considered. These results are consistent with the fact that in the absence of H_2 , TiCl_4 can not be reduced to supply Ti to the solid phase. On the other hand, C can be deposited through

species such as CH_3Cl and CH_2Cl , formed from hydrocarbon radicals and Cl from the disproportionation of TiCl_4 . At higher temperature, the effect of the inert carrier is less pronounced as vapor species decompose more readily.

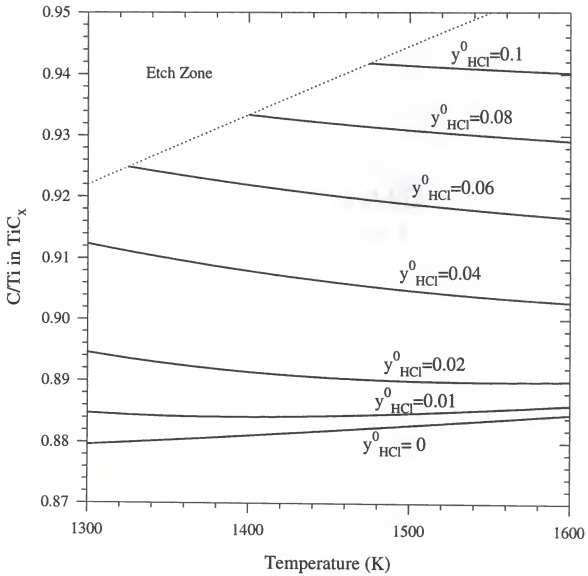
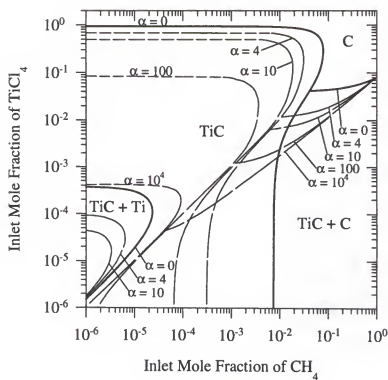
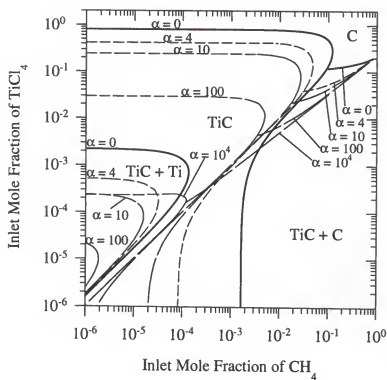


Figure 2.24 Effect of HCl addition to the reactant mixture on the TiC_x composition ($y_{CH_4}^0 = 10^{-3}$ and $y_{TiCl_4}^0 = 10^{-3}$).



(a)



(b)

Figure 2.25 Effect on the Ti-C-H-Cl CVD diagram of replacing H_2 with He ($\alpha = y_{He}^0 / y_{H_2}^0$).

a) $T = 1300$ K; b) $T = 1600$ K.

CHAPTER 3 GROWTH OF TiC_x BY CVD

3.1 Introduction

CVD has become an important method for the fabrication of ceramic coatings for a variety of applications. The successful application of CVD to deposit a given chemistry, however, requires an understanding of the underlying mechanisms governing the deposition process. By definition, CVD involves the growth of a solid material onto a substrate via the reaction of gaseous precursors at the gas-solid interface. This definition means that at the elementary level, CVD can be viewed as the result of a combination of surface reaction and mass transfer processes. A boundary layer model is often used to describe CVD as a series of sequentially-linked steps leading to deposition of the coating [219]. Figure 3.1 illustrates the steps in this simplified model, which can be summarized by the following mechanistic elements: 1) forced flow of the reactants over the substrate, 2) diffusion of the reactants through the boundary layer, 3) adsorption of the species onto the substrate, 4) chemical reaction, surface diffusion, and inclusion into the growing film of the adsorbed species, 5) desorption of reactant and product species from the substrate, 6) diffusion of product or reactant species through the boundary layer to the bulk gas flow, and 7) forced flow of gases out of the reaction zone. In view of the sequential nature of the steps, the rate of the overall growth process will be controlled by the slowest step in the sequence. Two operational regimes commonly arise as a consequence: one where

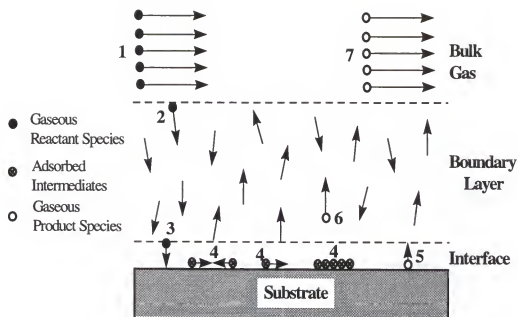


Figure 3.1 Elementary processes underlying CVD [219].

kinetic or surface steps are limiting, the other where mass transfer steps (primarily diffusion) are the slowest. While kinetic processes are typically characterized by a stronger dependence on temperature relative to diffusion, heterogeneous kinetic steps are insensitive to changes of the overall flow rate, but sensitive to the substrate crystallographic orientation. On the other hand, diffusion is affected by the overall flow rate through the influence of the gas velocity (v) on the boundary layer thickness (typically $\propto v^{1/2}$), and insensitive to the substrate crystallographic orientation. Consequently, a transition from a kinetics controlled to a diffusion controlled growth mechanism is often observed as the growth temperature is increased, and vice-versa as the overall flow rate is increased. In the transition regime between these limits, the growth process is a complex convolution of both mechanisms.

While CVD processes can be operated successfully in either regime, CVI processes are most effective in the kinetically controlled growth regime. Since CVI is

simply CVD inside a porous medium, it is important that diffusion be faster than the reactions occurring on the pore walls to achieve uniform deposition throughout the porous material. It is, therefore, desirable to study the deposition kinetics of the chemistry used for infiltration. Study of the chemistry on flat substrates under kinetically controlled conditions simplifies this task.

In this chapter CVD of TiC_x from $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ mixtures on the substrates Nicalon (SiC-O fibers), SiO_2 , Ta, Mo, graphite and polycrystalline and single-crystal Al_2O_3 is explored. Operating conditions resulting in reaction-controlled growth were determined, and the influence of temperature, flow rate, and precursor composition on the growth rate was examined. In addition, this study examined the effect of addition of HCl to the reactant mixture on the reaction rate. As a companion study, the effect of deposition parameters on the solid composition and surface morphology was also investigated.

3.2 Previous Work on TiC_x Deposition Mechanisms

Thermal CVD of TiC_x is commonly performed with a chloride chemistry using TiCl_4 and saturated hydrocarbon precursors. CH_4 is easily transported, available in high purity, and the rate of thermal decomposition is expected to be relatively rapid. The latter assumption was confirmed by Teyssandier who compared the rate of deposition of TiC_x on Mo substrates using either CH_4 or C_3H_8 as the carbon source [236]. The deposition rate using CH_4 was found to be approximately three times that using C_3H_8 .

Deposition of TiC_x from $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ mixtures has been most extensively studied on steel, cemented carbides and cermets substrates [154,162]. The reported

deposition rates of TiC_x on these substrates are relatively high compared to inert substrates, and this is attributed to the participation of carbon from the substrates on formation of the coating [24,26,106,107,108,162]. It is also theorized that the elements Fe, Ni and Co, present in these substrates, play a role in enhancing the growth rates by either reducing the activation energy for carbon diffusion from the substrate, or catalyzing the decomposition of the gaseous hydrocarbon precursors [106,108,154].

Studies on the effect of deposition parameters on the growth rate have been reported. Stjernberg et al. measured the influence of inlet CH_4 , TiCl_4 and HCl partial pressures on the growth rate of TiC_x at 1000°C [162]. Lindstrom and Amberg reported that the deposition rate of TiC_x was independent of total flow rate, suggesting a growth process controlled by surface reactions [237]. They concluded that TiCl_4 decomposition occurs by heterogeneous reaction and parallel homogeneous disproportionation to form titanium sub-chlorides and HCl . Cho and Chun studied primarily the influence of CH_4 partial pressure on the growth rate and decarburization of the substrate as they have concentrated on the deposition of TiC_x on cemented carbides.

Two different mechanisms have been proposed to explain the influence of deposition parameters on the growth rate on inert substrates. Stjernberg et al., have proposed a two-site Langmuir-Hinshelwood mechanism of reaction where the larger Ti atoms adsorb on one site while the C and Cl atoms compete for the remaining available sites [162]. Since they identified the adsorption of CH_4 as rate limiting, this explains the inhibiting effect that HCl , from TiCl_4 or intentionally added, has on the reaction rate. More recently, Haupfear and Schmidt have completed an extensive study of the kinetics of TiC_x deposition from TiCl_4 - C_3H_8 - H_2 mixtures on W using in-situ differential

gravimetry [163]. Their results point, conclusively, to a one-site Langmuir-Hinshelwood mechanism with competitive adsorption between TiCl_4 and C_3H_8 ; however, they did not consider the affect of added HCl. The work of Cho and Chun indicates that the one-site mechanism may be applicable to the $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ system as well [102]. They observed that the growth rate exhibits a maximum with the partial pressure of CH_4 which is a behavior characteristic of one-site competitive mechanisms. The fact that the substrate was a cemented carbide makes this evidence rather inconclusive, in view of the complex influence of substrate carbon on the kinetics.

3.3 Experimental Apparatus and Procedure

A schematic of the multichemistry CVD system used to deposit the coatings is shown in figure 3.2. The system, which was designed and constructed as part of this project, consisted of four compressed precursor gas sources and three liquid precursor sources. Reactant mixtures were delivered to the reactor through either of two independent flow channels where they were diluted in flows of either Ar or H_2 . Two other flow channels were provided to supply additional Ar/ H_2 for further dilution of the precursors in the reactor, or to flush the reactor during rapid switching-flow operations. Metering of the compressed gas flowrates was accomplished by means of mass flow controllers (MKS model 1159B). To deliver the liquid sources to the reactor a carrier gas was bubbled through the column of liquid, and saturated with the precursor source. To control the vapor pressure of the liquid, the bubblers were immersed into constant temperature baths (VWR model 1155), while control of the bubbler pressures was achieved by measuring the pressure at the inlet and regulating the outlet flow with

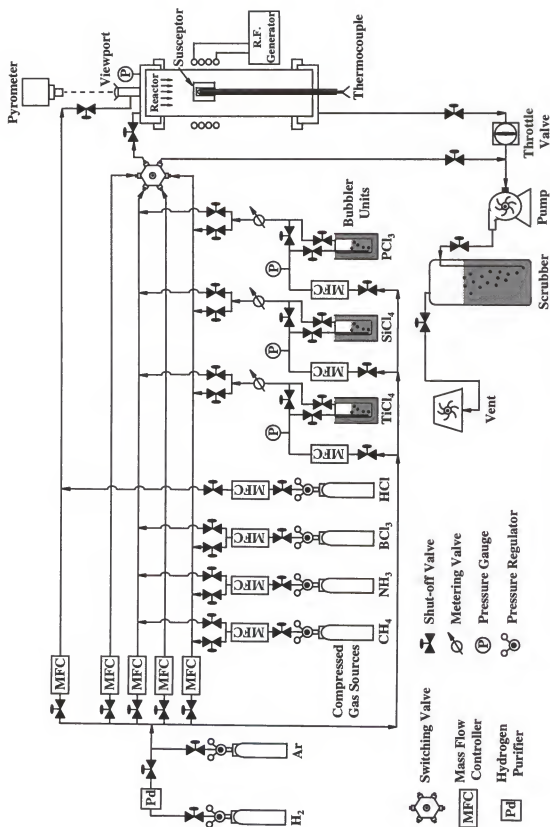


Figure 3.2 Schematic diagram of multichemistry CVD system.

metering valves. With the assumptions of saturation and ideal gas behavior the liquid precursor flow can be calculated from the following equation:

$$F_i = F_{H_2} \left(\frac{P_i^{sat}}{P_t - P_i^{sat}} \right)$$

where F_i is the flow rate of the liquid precursor (e.g., $TiCl_4$), F_{H_2} the flowrate of the carrier gas H_2 , P_i^{sat} the vapor pressure of the liquid precursor at the bubbler temperature, and P_t the total bubbler pressure. Depositions occurred inside a vertical, 76 mm diameter quartz reactor that was o-ring sealed at both ends by water-cooled flanges. The substrates were supported by a cylindrical graphite pedestal susceptor, and heated by induction of the susceptor with a 7.5 kW Westinghouse rf generator. Substrate temperature was measured from both the bottom with a sheathed type-S thermocouple placed inside the susceptor approximately 3 mm from the substrate, and the top with a two-color optical pyrometer (Capintec model ROS-8) focused through a gas-swept quartz viewport. The thermocouple output was also used for temperature control. The pressure in the reactor was regulated by a control loop consisting of a pressure gage (MKS Baratron 221A) upstream and a throttle valve (MKS model 253A) downstream from the reactor. The gases exiting the reactor were first passed through an ice cooled trap to condense the Ti sub-chloride species. The remaining gases were then treated in a scrubber unit, containing a 20% NaOH solution, prior to venting the gas stream to the atmosphere. The system was generally operated at atmospheric pressure, but it was also capable of low pressure operation (as low as 1 Torr) by means of a rotary vacuum pump (Leybold model D32C). The pressure, temperature and flow controls of the system were all automated and operated via computer.

Ultra high purity (UHP) grade H_2 and CH_4 , and 99.999% purity $TiCl_4$ were used as the reactant sources. In addition, UHP grade Ar was provided as an inert gas to purge the system. Typical operation involved introduction of the substrates to the reactor, followed by flushing of the reactor chamber with Ar under vacuum for 15 minutes. The reactor was then back-filled with H_2 , and the pressure of the system stabilized at the desired set-point. After this, the susceptor was heated to the operating temperature, and held there under H_2 flow for 10 minutes to allow the substrates to reach thermal equilibrium. Precursors flows were next started to begin growth of the coating which occurred for times ranging from 0.5 to 8 hours. After completion of the preset growth time, the precursor flows were stopped, but the substrates were maintained at the growth temperature under H_2 flow for 10 minutes to allow purging of the reactants remaining in the system lines. Finally, the reactor was cooled to room temperature, and flushed under vacuum with argon, prior to opening it to ambient to remove the samples.

All experiments were performed at atmospheric pressure, and the reactant partial pressures were in the range of 50 to 8100 Pa for CH_4 and 10 to 2030 Pa for $TiCl_4$. The total flow rate of gases varied from 250 to 2000 sccm, while the deposition temperatures ranged from 1173 to 1573 K. Substrates consisted of disks of Nicalon (SiC-O) 12-harness satin weave cloth (Dow Corning), planar samples of SiO_2 (Dow Corning), 10 μ m grit polished graphite (Union Carbide), 1 μ m grit polished foils of Mo and Ta (Johnson Matthey), electronic grade polycrystalline Al_2O_3 (Commercial Crystal Laboratories), and single crystal (0001) and (1 $\bar{1}$ 02) Al_2O_3 (Commercial Crystal Laboratories). All substrates, except for the Nicalon weave preforms, were degreased and cleaned by

sonication in acetone for 2 minutes before deposition. In addition, the graphite samples were baked for 10 hours at 80 °C in order to thoroughly dry them.

Approximately 200 films of TiC_x were deposited, the majority on polycrystalline and single crystal Al_2O_3 and Nicalon weave preforms. The average growth rate of TiC_x on the planar substrates was determined by measuring the weight change of the substrates over the deposition time, and normalizing by the exposed surface area (i.e., neglecting the sides and bottom surface). Because of the difficulties of estimating the internal surface area of the Nicalon preforms, an apparent rate of deposition on these samples was calculated using the area projected by the top surface of the preforms.

A scanning electron microscope (SEM) was used to observe the surface morphology deposited coatings. The samples for SEM consisted of fracture planes and 0.25 μm grit polished cross-sections of infiltrated weaves and planar samples, cast in acrylic or epoxide resins. To prevent charging at the surface during SEM analysis, all samples were coated with Au/Pd. In addition, the coatings were analyzed by x-ray diffraction (XRD), electron probe microanalysis (EMPA) and auger electron spectroscopy (AES) to obtain information on crystallinity, preferred orientation and elemental composition. For EMPA measurements special care was taken to avoid carbon contamination on the samples during polishing or other preparation steps.

3.4 Results and Discussion

3.4.1 Effect of Deposition Parameters on the Deposition Rate

The influence of the total flow rate on the growth rate of TiC_x on polycrystalline Al_2O_3 was investigated at 1573 K and a reactant partial pressures of 1020 Pa for CH_4 and

1010 Pa for TiCl_4 . Figure 3.3 shows a plot of the average deposition rate versus the square root of the total flow rate. The growth rate increases linearly up to approximately 926 sccm, becoming constant at a value that varies with the temperature and reactant partial pressures, for higher flow rates. A similar study of the growth rate (figure 3.3) on single crystal Al_2O_3 substrates reveals the same transition in the growth rate dependence at 999 and 1027 sccm for (0001) and (1 $\bar{1}$ 02) Al_2O_3 respectively. Under mass transfer limitation, the growth rate should exhibit a linear dependence with the square root of the average gas velocity, which is proportional to the total flow rate. Thus, it is evident that the boundary between mass transfer and reaction-limited growth lies on average at a flow rate of 984 sccm for these substrates. In all of these cases, the curves relating the growth rate to the gas flow rate do not pass through the origin. This indicates that deposition can not be obtained below a threshold flow where mass transfer limitation forbids any measurable growth.

The temperature dependence of the deposition rate on polycrystalline Al_2O_3 was determined at constant reactant partial pressures of 2020 Pa for CH_4 and 2020 Pa for TiCl_4 , and a total volumetric flow rate of 1000 sccm. To quantify the apparent rate of deposition, the substrate weight increase was plotted as a function of the deposition time for various temperatures, and the growth rate obtained from the slope of the weight change curves (figure 3.4). Each of the weight gain curves extrapolated to a value of zero at the beginning of growth for each temperature, indicating no significant nucleation limitation. A plot of the apparent growth rate versus the reciprocal temperature (figure 3.5) reveals an Arrhenius dependence of the growth rate with an apparent activation

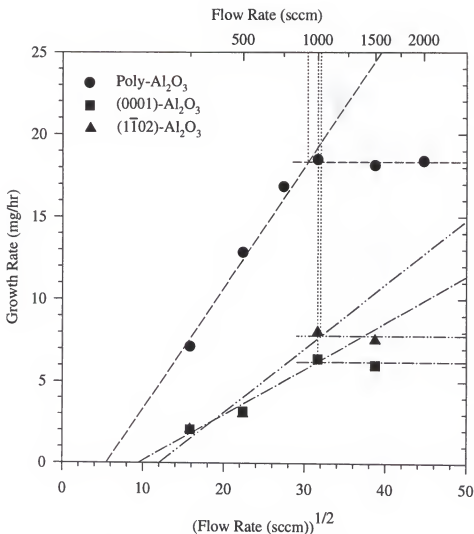


Figure 3.3 Effect of the total gas flow rate on the growth rate of TiC_x polycrystalline Al_2O_3 at 1573 K.

energy of 137 ± 9 KJ/mol. A similar analysis was performed on (0001) and (1 $\bar{1}$ 02) single crystal Al_2O_3 at reactant partial pressures of 2020 Pa for CH_4 and 1010 for TiCl_4 , and a flow rate of 1000 sccm. Depositions on both substrates occurred in the same experimental run. The weight gain curves are shown in figure 3.6, and the resulting Arrhenius plot in figure 3.7. The calculated apparent activation energies were 284 ± 34 KJ/mol and 328 ± 45 KJ/mol for deposition on (0001) and (1 $\bar{1}$ 02) Al_2O_3 , respectively.

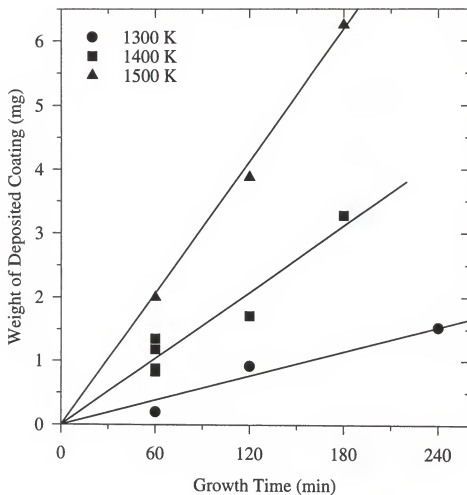


Figure 3.4 Weight of TiC_x deposited on polycrystalline Al_2O_3 as a function of deposition time at 1300 K, 1400 K and 1500 K.

The effect of temperature on the growth rate of TiC_x on Nicalon preforms, graphite and Ta was also investigated. The reactant partial pressures and total flow rate were the same as those used with single crystal Al_2O_3 . The corresponding Arrhenius plots are shown in figure 3.8. The calculated activation energies were 210 ± 15 KJ/mol for Nicalon, 89 ± 11 KJ/mol for graphite and 81 ± 24 KJ/mol for Ta. Insufficient data were obtained to report activation energies for depositions of TiC_x on Mo and SiO_2 . In table 3.1, the activation energies obtained in this study are compared to other previously reported values. Clearly, the variations in activation energies with substrate type and the

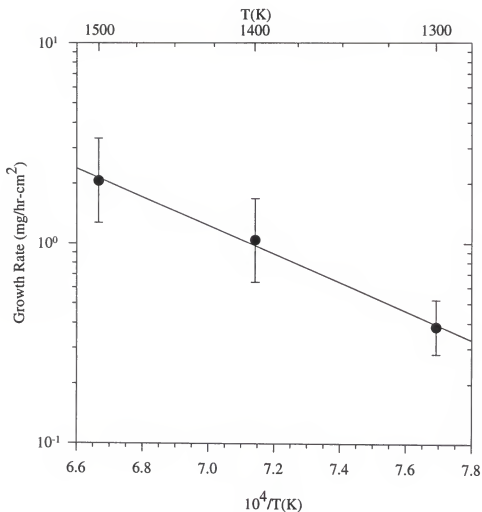


Figure 3.5 Arrhenius plot of the growth rate of TiC_x on polycrystalline Al_2O_3 .

transition growth regime with the total gas flow rate points to a reaction-limited mechanism for the growth of TiC_x under the considered conditions. Specifically, for depositions of TiC_x on polycrystalline, (0001) and (1 $\bar{1}$ 02) Al_2O_3 the growth mechanism is reaction-limited at total gas flow rates above 1026 sccm and growth temperatures below 1278 K. It is obvious from table 3.1 that a large range of activation energies have been observed for the deposition of TiC_x . Thus, differences in surface chemistry between different substrate materials and orientations of substrates of the same materials are reflected in the contrasting activation energies and coating surface morphology.

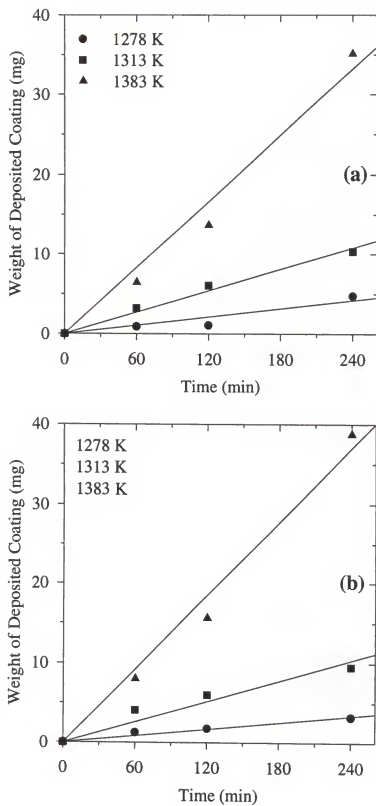


Figure 3.6 Weight of TiC_x deposited on single crystal Al_2O_3 at 1278 K, 1313 K and 1383 K.

a) (0001) Al_2O_3 ; b) (1 $\bar{1}$ 02) Al_2O_3 .

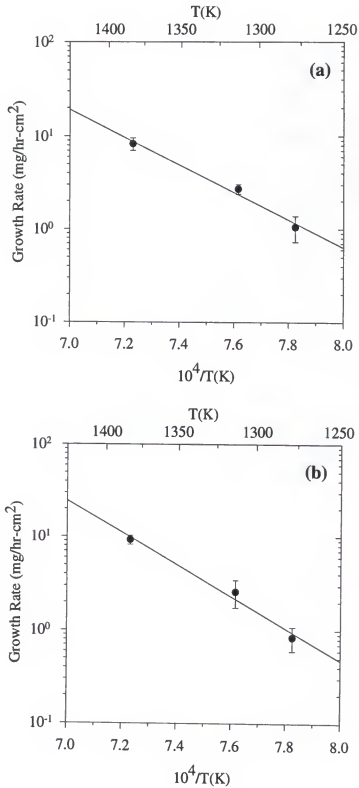


Figure 3.7 Arrhenius plots of the TiC_x growth rate on single crystal Al_2O_3 at 1278 K, 1313 K and 1338 K.

a) (0001) Al_2O_3 ; b) (1 $\bar{1}$ 02) Al_2O_3 .

the differences in surface chemistry caused by varying grain orientations and atomic bonding in the substrate should affect the nucleation process, and thus, should reflect in contrasting activation energies and coating surface morphology (as discussed later).

The effect of CH_4 partial pressure on the growth rate is shown in figure 3.9. The deposition temperature and the TiCl_4 partial pressure were held constant at 1383 K and 1010 Pa, respectively. The slope of the curve was found to be 1.06 ± 0.06 , indicating a first-order dependence of the growth rate on the CH_4 partial pressure. This result is consistent with work by Stjernberg et al., who proposed a Langmuir-Hinshelwood mechanism (see section 3.2) in which the growth rate also follows a first-order dependence on the CH_4 partial pressure [162]. Because of this trend, CH_4 pyrolysis has been postulated as the rate-limiting step in the deposition of TiC_x [24]. Vandenbulcke has suggested that kinetic limitations, due to the decomposition of CH_4 , explains the departure from equilibrium of the TiC_x composition when deposited with this source [166]. The observed closer agreement between experimental and equilibrium values of the carbon content when C_3H_8 was used is consistent with increasing decomposition rates for higher paraffins and the associated lower activation energies. Lee and Richman have also postulated a rate limitation due to pyrolysis of the hydrocarbon source [24]. In their study, where toluene was used as carbon precursor, the resulting activation energy of deposition was 368 KJ/mol which agrees well with the independently measured activation energy of heterogeneous toluene pyrolysis (376 KJ/mol). In this study, although, there is agreement between the activation energy of heterogeneous CH_4 pyrolysis (312 KJ/mol) and the activation energies of TiC_x deposition on single crystal Al_2O_3 , this is not the case for other substrates [238]. In addition, as pointed by Lee and

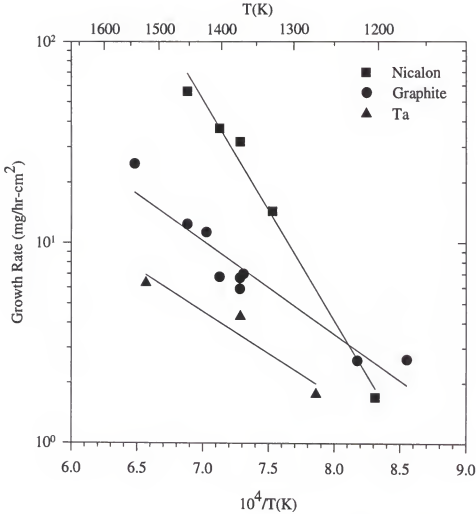


Figure 3.8 Arrhenius plots of the TiC_x growth rate on Nicalon, graphite and Ta.

Richman, hydrocarbon for decomposition does not always correlate with reaction limitations in the deposition process [24]. While they found progressively lower activation energies for the pyrolysis of CH_4 , C_2H_6 and C_3H_8 , Takahashi et al. [104] have reported higher deposition rates of TiC_x using C_2H_6 compared to C_3H_8 , and Teyssandier [236] has observed rates three times higher using CH_4 than C_3H_8 . The Langmuir-Hinshelwood mechanisms proposed by Stjernberg et al. should also be reevaluated in view of results by Cho and Chun on cemented carbides substrates [102] and

Table 3.1 Comparison of Activation Energies for TiC_x Deposition using TiCl_4 as a source.

Substrate	Ea (KJ/mol)	Hydrocarbon Source	Pressure (Atm)	Reference
WC-Co	351-393	C_3H_8	1	26,104
WC-Co	276	CH_4	1	110
WC-Co	184	CH_4	1	104
WC-Co	372	CH_4	1	236
WC-Co	108	none	1	236
Graphite	418	CH_4	0.132	57
Graphite	159	CH_4	1	110
Graphite	84	none	1	117
Graphite	100	none	1	238
Porous Graphite	62	none	1	239
Pseudocrystal Graphite	71	none	1	239
Steels	201	CH_4	1	240
Mo	192	CH_4	1	117
W	80-88	C_3H_8	1.3×10^{-5} - 6.6×10^4	165
Polycrystalline Al_2O_3	137	CH_4	1	this study
(0001) Al_2O_3	284	CH_4	1	this study
(1 $\bar{1}$ 02) Al_2O_3	328	CH_4	1	this study
Nicalon	210	CH_4	1	this study
Graphite	89	CH_4	1	this study
Ta	81	CH_4	1	this study

Konyashin on Al_2O_3 substrates, who found that the growth rate of TiC_x can also decrease with increasing inlet CH_4 partial pressure [154].

The effect of the TiCl_4 partial pressure on the growth rate is shown in figure 3.10. The deposition temperature and CH_4 partial pressure were held constant at 1383 K and 506 Pa, respectively. The growth rate is observed to increase with TiCl_4 partial pressure at low inlet partial pressure, reach a maximum just below the 1:1 stoichiometric composition, and then decrease monotonically. This behavior has also been noted by Jang and Chun who studied the deposition of TiC_x on various steels [107]. Lindstrom and Amberg, on the other hand, found an inverse dependence of the deposition rate with the

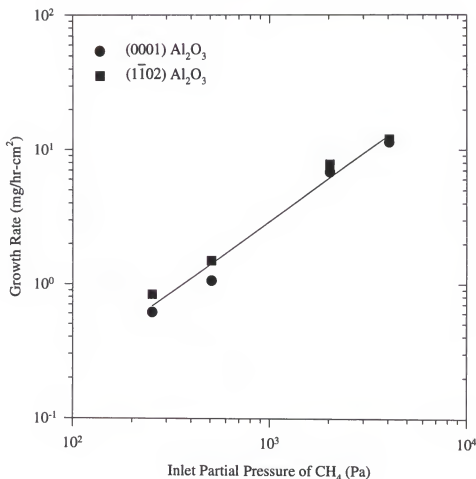


Figure 3.9 TiC_x growth rate on single crystal Al_2O_3 as a function of the CH_4 partial pressure at 1383 K and $P_{\text{TiCl}_4}^0 = 1010$ Pa.

TiCl_4 partial pressure. In this work, they only examined two concentrations of TiCl_4 [237]. Stjernberg et al., also reported an inverse relationship which they explained with a two-site adsorption model where chlorine and carbon atoms compete for the same site [162]. They postulated that TiCl_4 reaches rapid homogeneous equilibrium with its subchlorides, and the HCl thus formed inhibits the adsorption of carbon-containing species. Haupfear and Schmidt have performed the most comprehensive study of the kinetics of TiC_x deposition using C_3H_8 and TiCl_4 precursors [163]. They found that the rate of deposition exhibits a maximum in both the C_3H_8 and TiCl_4 concentrations

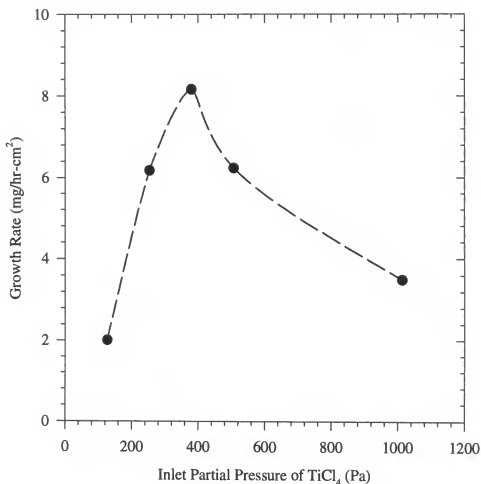


Figure 3.10 Growth rate of TiC_x on (0001) Al_2O_3 as a function of the TiCl_4 partial pressure at 1383 K and $P_{\text{CH}_4}^0 = 506$ Pa.

suggesting a one-site competitive adsorption mechanism of both Ti and C. They ignored, however, the adsorption of Cl. The same behavior has been reported for the deposition rate of SiC from $\text{SiCl}_4\text{-CH}_4\text{-H}_2$ [194]. Because of the similarities in chemistry, it can be inferred that a similar mechanism exists in the deposition of TiC_x from CH_4 and TiCl_4 . This would explain the findings in this study and the contrasting results of other reports. Obviously, at low concentrations of the precursors, the rate would behave proportionally to changes in their partial pressures whereas at high concentrations an inverse relationship would be observed. Since all these studies consider only a small

range of concentration values, it is apparent why some authors report one type of dependence while others report the opposite.

The influence of HCl addition to the reactants on the growth rate of TiC_x has received little study. Stjernberg et al. reported a decrease in the growth rate with increasing HCl input. At an input HCl concentration of 5 vol. %, no deposition was observed with etching of the Al_2O_3 substrate by the HCl [162]. Similar inhibiting effects by adding HCl have also been seen with other CVD halide chemistries. HCl, in concentrations as low as 1%, has been reported to reduce the deposition rate of W, from $\text{WF}_6\text{-H}_2$ mixtures, by as much as 50 % [242]. In other studies, 7% added HCl has been found to almost completely stop the deposition of B from $\text{BCl}_3\text{-H}_2$ reactants [243].

The influence of HCl on the deposition rate of TiC_x was also investigated in this study, and it is shown in figure 3.11. The temperature and reactant partial pressures were held constant at 1383 K and 506 Pa for both CH_4 and TiCl_4 , respectively. The growth rate is seen to have an inverse dependence with the added HCl concentration up to 200 Pa. Beyond 200 Pa, however, the deposition rate appears to become insensitive to further increase in the HCl concentration. This stabilization behavior could be attributed to the etching of the graphite susceptor which results in the production of additional carbon-containing vapor species. The increased concentrations of these species would then be expected accelerate the deposition rate, thus balancing the HCl effect.

3.4.2 Composition of TiC_x Films

A series of experiments was also performed to determine the effect of reactant inlet composition on the films stoichiometry. In figures 3.12 and 3-13, measured C/Ti

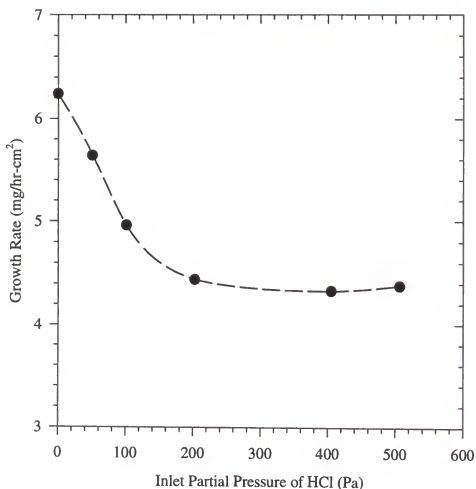


Figure 3.11 Growth rate of TiC_x on (0001) Al_2O_3 as a function of added HCl partial pressure at 1383 K, $P_{\text{CH}_4}^0 = 506 \text{ Pa}$ and $P_{\text{TiCl}_4}^0 = 506 \text{ Pa}$.

ratios of films deposited on polycrystalline Al_2O_3 are compared with the calculated equilibrium values presented in section 2.6.2 (see figures 2.13-2.16). In figure 3.12, the deposition temperature and TiCl_4 partial pressure were held constant at 1500 K and 1013 Pa, respectively. The C/Ti ratio was measured by calculating the lattice parameter of the films from XRD data and using Storms' correlation between the TiC_x stoichiometry and the lattice parameter. The reproducibility of the film composition on different samples for a given set of operating parameters is seen to be excellent. The carbon content of the films increased with increasing CH_4 partial pressure as expected.

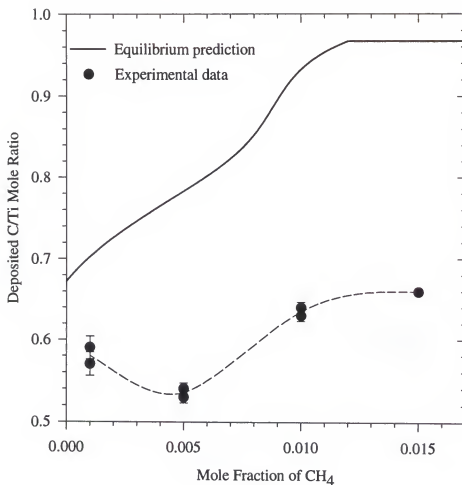


Figure 3.12 Comparison of equilibrium and measured C/Ti ratios of films deposited on polycrystalline Al_2O_3 at 1500 K and $P_{\text{TiCl}_4}^0 = 1013 \text{ Pa}$.

The predicted equilibrium C/Ti molar ratio with CH_4 partial pressure was considerably greater than observed and there was a stronger CH_4 partial pressure dependence than was predicted. For the data shown in figures 3.13a and b, the deposition temperature was 1400 K, and the TiCl_4 partial pressure was 1013 Pa and 10 Pa, respectively. The C/Ti ratio was measured by both AES and EMPA, using in both cases a standard sample of known composition. EMPA results were not reported in figure 3.13b as the films were too thin for the technique to gather statistically meaningful data. The results shown in figure 3.13a again show that the carbon content in the films increased with increasing CH_4 inlet

mole fraction, but there remain discrepancies between the data and the predicted values, particularly at the lower inlet CH_4 concentrations. At the highest CH_4 mole fraction studied ($y_{\text{CH}_4}^0 = 0.08$), the observed C/Ti ratio is lower than the expected trend. This can be attributed to scattering of the measured signal from the coating by the film surface roughness which worsens at the higher reactant concentrations due to the resulting enhanced growth rates. In figure 3.13b, the carbon content of the films shows a maximum with increasing CH_4 concentration. In this case, surface roughness did not account for the reduced C/Ti ratios at high CH_4 mole fractions. As with the results of figure 3.13a, there was a large difference between the equilibrium results and the experimental data.

For the films deposited on both types of single crystal Al_2O_3 substrates, the measured composition remained constant ($\text{C/Ti} = 0.52$) as the inlet ratio of CH_4 to TiCl_4 partial pressures was varied from 0.25 to 4.0. The apparent independence of the film composition on the inlet gas concentration ratio was again attributed to errors in the EMPA measurements caused by the film surface roughness. Improvements in the measurements could not be achieved by polishing because of poor adhesion of the films to the substrates.

The composition of the films deposited onto graphite and Nicalon was also determined by EMPA. For these films, cross-sections of the samples were cast and polished to reduce measurement errors. At a deposition temperature of 1500 K and reactant partial pressures of 2026 Pa for CH_4 and 1013 for TiCl_4 , the deposited C/Ti ratio was the same (0.92) on both substrates. As the partial pressure of CH_4 was increased to 3544 Pa, the C/Ti ratio increased to 1.07, suggesting the formation of free carbon. These results correlate substantially better with equilibrium calculations. According

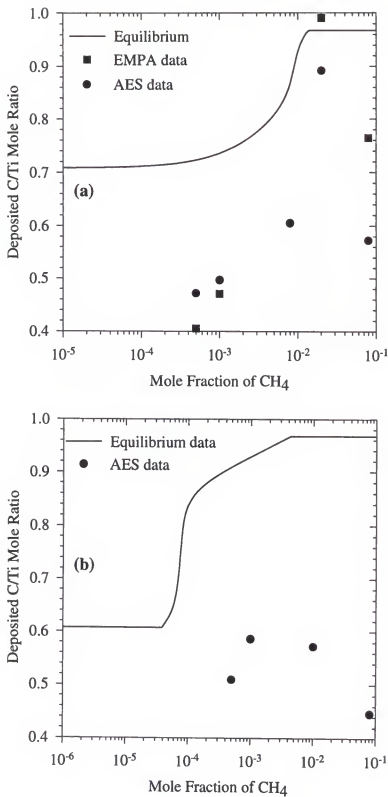


Figure 3.13 Comparison of equilibrium and measured C/Ti ratios of films deposited on polycrystalline Al₂O₃ at 1400 K.
 a) $y^0_{\text{TiCl}_4} = 10^{-2}$, b) $y^0_{\text{TiCl}_4} = 10^{-4}$.

to equilibrium calculations shown in figure 2.16, the reactant inlet compositions used to grow both of these samples should produce $\text{TiC}_x + \text{C}$ two-phase films with the C/Ti ratio in the carbide remaining constant at 0.97. Therefore, the first measurement is slightly lower than the predicted value, while the second suggests the existence of two phases and thus agrees with the equilibrium results. At 1300 K and reactant partial pressures of 2026 Pa of CH_4 and 1013 Pa of TiCl_4 , the films on both substrates become richer in Ti, with an elemental ratio of 0.82. This measurement, on the other hand, disagrees with the expected elemental ratio of 0.97.

The discrepancies between equilibrium and experimental results can be explained in part by errors in the measurements, either due to surface roughness, or insufficient film thickness. Discrepancies of this order have been reported by others [25,166], and are likely a the result of kinetic limitations imposed by the relative thermal stability of CH_4 [24,166]. Accordingly, in studies where C_3H_8 was used as carbon source, there has been substantially better agreement between equilibrium predictions and experimental results, as anticipated from the lower activation energy of C_3H_8 decomposition.

3.4.3 Surface Morphology and Grain Orientation of TiC_x Films

The substrates examined in this work have a wide range of chemical compatibility with TiC_x . Graphite is a semimetal, and since carbon is a component of the TiC_x solid solution, it is an additional reactant source besides the gas phase hydrocarbon. Mo and Ta are refractory metals which can form stable carbide compounds during the initial stages of growth. Al_2O_3 and SiO_2 are insulators which are relatively inert in the presence of TiC_x . The properties of Nicalon (SiC-O) are close to those of SiC and thus similar to

TiC_x. As expected, quite dissimilar grain orientations and surface morphologies were observed for different substrates.

The reactor geometry used for growth of TiC_x on Nicalon was different than that for other substrates (see chapter 5). In this case, a temperature gradient was imposed across a stack of Nicalon weave disks, and due to the preform-susceptor arrangement significant mass transfer limitations resulted in the inner portions of the stack. As discussed in chapter 5, this arrangement is typical of a type II CVI process, i.e., thermal gradient-isobaric CVI [36]. As the deposition temperature increased from 1273 K to 1473 K, the surface morphology of the TiC_x deposited on Nicalon fibers changed from pyramidal needles 0.2 to 1 μm in size to more rounded, equiaxed grains smaller than 0.2 μm (figure 3.14). Fracture sections of the coating showed that at the lower deposition temperatures the deposit grains were columnar and aligned perpendicular to the fiber surface (figure 3.15).

Nodular growth, characteristic of high growth rate, was observed on fibers closest to the gas inlet. In this area, locally accelerated deposition occurs although this fiber location was at the lowest temperature. The nodules consisted of blocky crystals with step-ledge like features which are markedly different from the deposits obtained on most of the fiber surface (figure 3.16). Since mass transfer is not believed to limit growth in this region of the preform, these nodules are not attributed to local gas phase disturbances, but rather to the nucleation pattern [244]. This surface morphology could result from accelerated nucleation induced by specific sites on the fiber surface and the high supersaturation of TiCl₄. Accordingly at lower TiCl₄ concentrations, these nodular growths were absent.

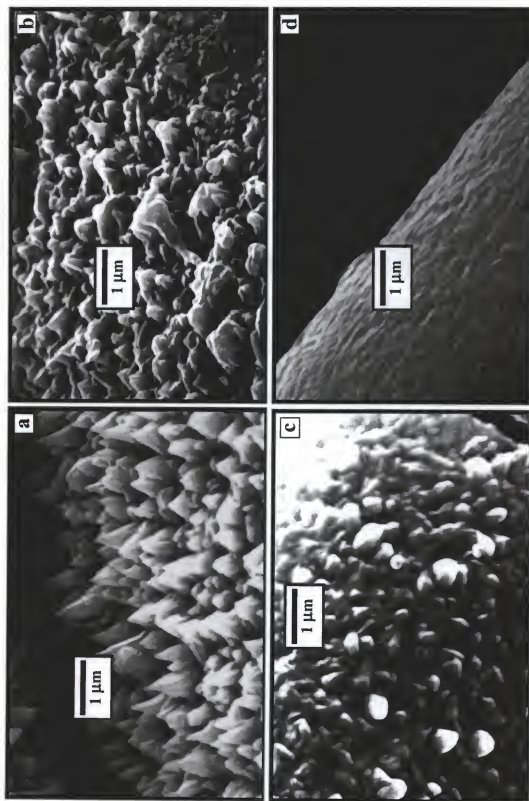


Figure 3.14 Effect of deposition temperature on the surface morphology of TiC_x deposited on Nicalon fibers.
a) 1273 K; b) 1123 K; c) 1373 K; d) 1473 K.

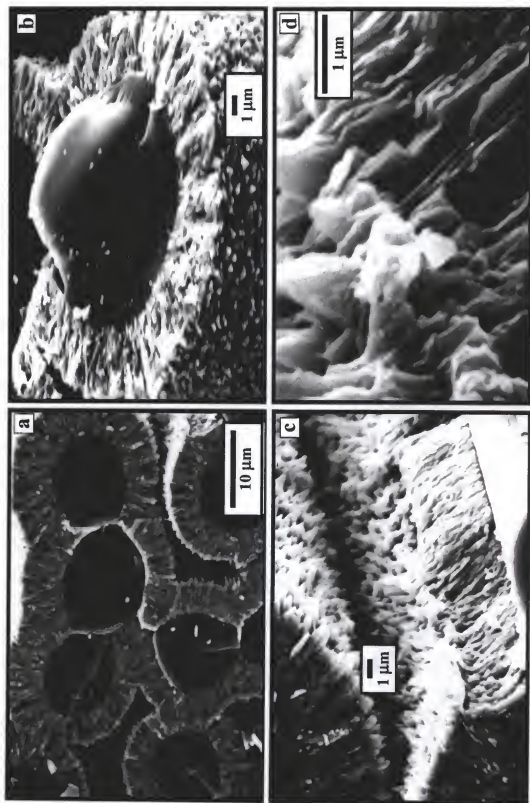


Figure 3.15 Microstructure of TiC_x deposited on Nicalon fibers at 1273 K.
a) 1600X; b) 4800X; c) 4800X; and d) 22000X magnification.

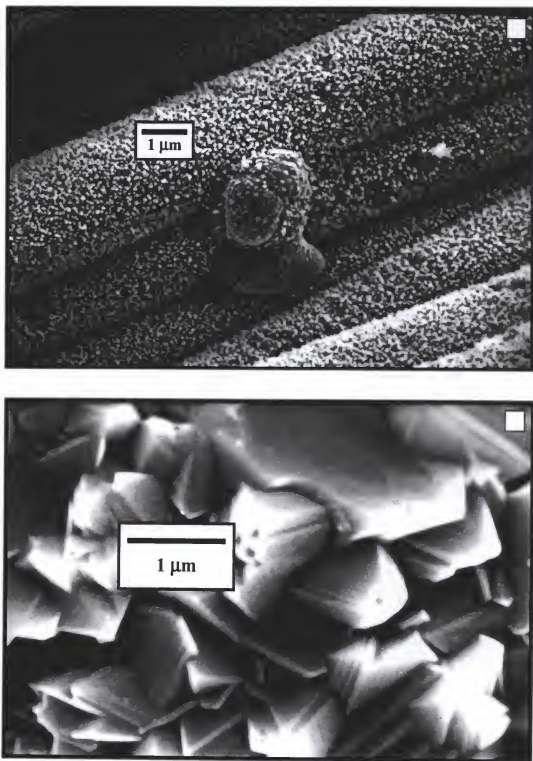


Figure 3.16 Nucleation nodes of TiC_x on Nicalon at 1323 K.
a) 1000X; b) 20000X magnification.

At deposition temperatures above 1473 K, a third type of surface morphology was observed on fibers located inside the graphite rings holding the Nicalon disks. In this region, the gas flow was greatly restricted, and the average temperature was higher than at any other point in the preform due to direct contact of the fibers with the inductively heated graphite rings. Superimposed on the fine grain structure of TiC_x observed on the majority of the fiber surface, 10-15 μm long whiskers with an aspect ratio of approximately 10 also formed (figure 3.17). In their study of Ni-catalyzed TiC_x deposition, Wukulski et al. [245] have reported whisker growth to occur at low reactant concentrations and system pressures. Apparently, TiC_x whisker formation on Nicalon is promoted by depletion of the reactants within restricted regions inside the graphite holder.

Despite these marked dissimilarities in surface morphologies, XRD patterns of both low and high temperature growths of TiC_x deposited on Nicalon are similar and correspond to that of nearly randomly oriented TiC_x (figure 3.19a). This observation is however not definitive since the sampling area of XRD is much larger than the features in figures 3-16 and 3-17, and since they represent only a small percentage of the total TiC_x deposit.

In contrast to, TiC_x films grown on Nicalon, those grown on graphite exhibited a dome-shaped structure. Magnification of films grown below 1273 K showed small needle-like aggregates 0.1 by $1\mu\text{m}$ in size (figure 3.18a). XRD indicated these needles were of random orientation (figure 3.19b). Transmission electron microscope (TEM) analysis of these structures showed that they were composed of grains with very diffuse, weakly defined boundaries, less than 30 nm in size. As the deposition temperature was increased, their shaped became more rounded and equiaxed grains appeared (figure

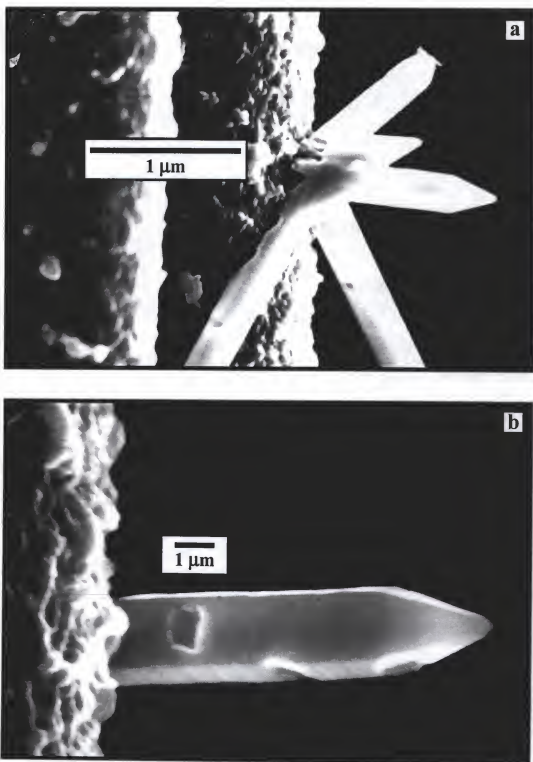


Figure 3.17 TiC_x whiskers formed in the space between the graphite rings ($T=1273\text{ K}$).
a) 3000X; b) 7800X magnification.

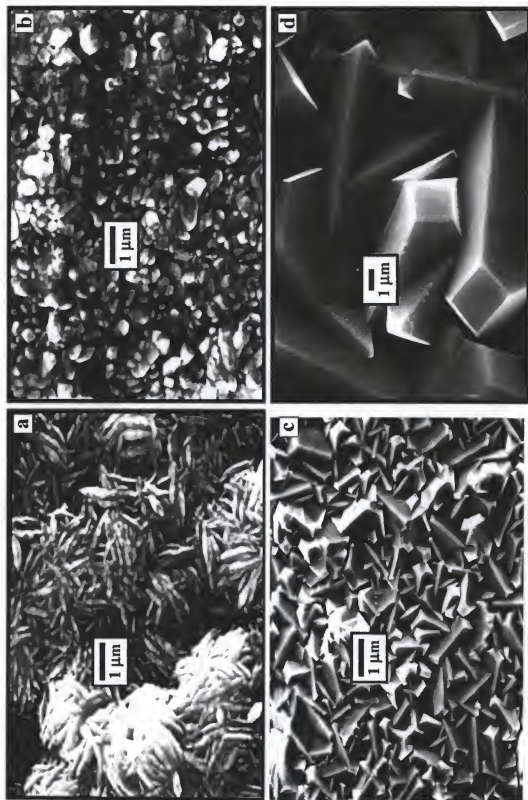


Figure 3.18 Surface morphology of TiC_x deposited on graphite.
a) 1273 K; b) 1373 K; c) 1473 K, 1000X; d) 1473 K, 5400X.

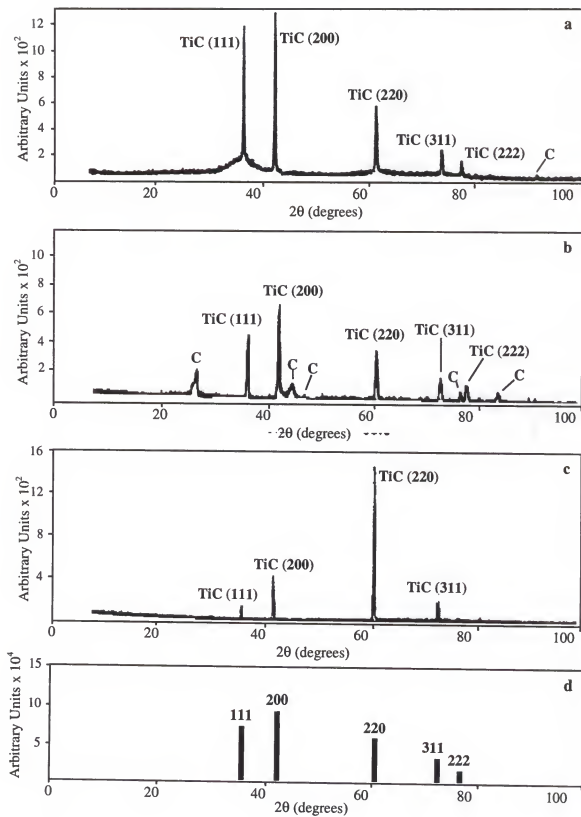


Figure 3.19 XRD patterns of TiC_x deposited on: a) Nicalon fibers at 1373 K; b) graphite at 1273 K; c) graphite at 1473 K; d) standard powder pattern.

3.18b). A further increase in temperature to 1473 K resulted in crystals with sharper edges forming blocky, faceted stacks 5 to 15 μm in size (figure 3.18 c,d). As the temperature increased, the films became more textured in a (220) orientation (figure 3.19c). Lee and Chun studied the deposition of TiC_x on cemented carbides using the same precursor chemistry as in this study [144]. They reported an insensitivity of the deposited film preferred orientation with deposition time and gas phase composition. Furthermore, they also observed a change in orientation from random at 1323 K to (220) between 1373 K and 1423 K.

TiC_x films deposited on fused SiO_2 at 1273 K were weakly bonded to the substrate. SEM analysis revealed knobby, amorphous-like particles less than 0.1 μm in size, covering larger, faceted crystallites (figure 3.21). The XRD peaks were broader, indicating a deterioration of the deposit crystalline quality (figure 3.22a). Preliminary, TEM measurements showed randomly oriented grains, up to several microns in size, with well developed boundaries. The randomness of the grain orientations is also confirmed by the XRD pattern.

The effect of the deposition temperature on the morphology of TiC_x films deposited on polycrystalline Al_2O_3 was opposite to that observed on graphite, Nicalon and SiO_2 . As the temperature was increased from 1273 to 1573 K, the TiC_x grain structure changed from a round, faceted shape to a needle-like form. On the other hand, the reactant composition had a converse effect. Figure 3.21 shows the surface morphology of TiC_x grown at increasing values of the $\text{CH}_4/\text{TiCl}_4$ inlet gas ratio. For Al_2O_3 as the substrate, the grains changed from an elongated, needle-like to equiaxed, faceted crystals. XRD analysis revealed a preferred (111) orientation for all films grown

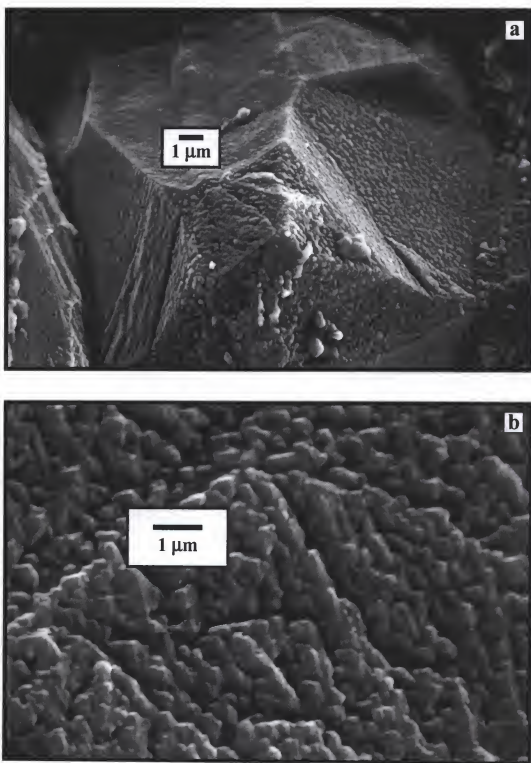


Figure 3.20 Surface morphology of TiC_x deposit on SiO_2 .
a) 5000X; b) 20000X magnification.

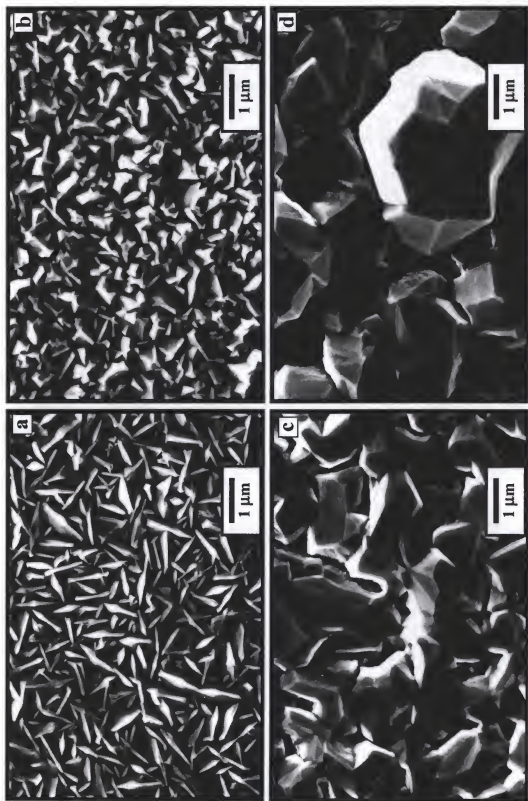


Figure 3.21 Influence of reactant ratio on the surface morphology of TiC_x deposited on polycrystalline Al_2O_3 at 1573 K.
a) $\text{CH}_4/\text{TiCl}_4 = 1$; b) $\text{CH}_4/\text{TiCl}_4 = 0.5$; c) $\text{CH}_4/\text{TiCl}_4 = 3$; d) $\text{CH}_4/\text{TiCl}_4 = 4$.

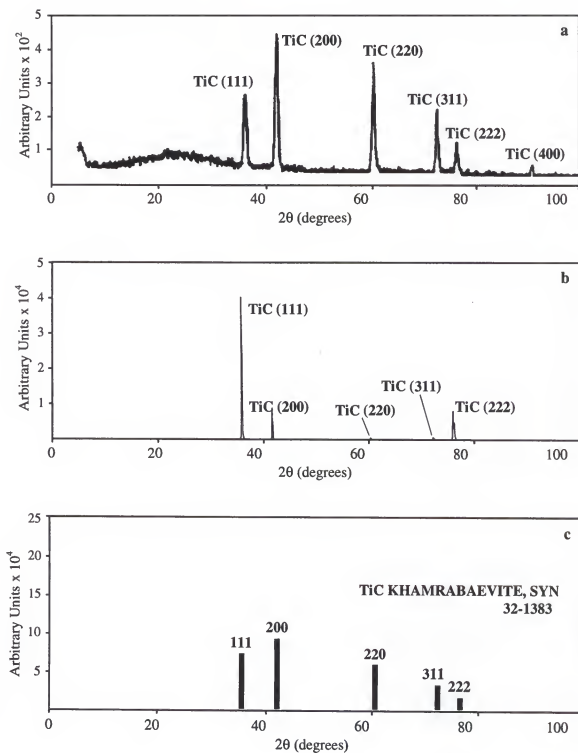


Figure 3.22 XRD patterns of TiC_x deposited on: a) SiO_2 at 1273 K; b) polycrystalline Al_2O_3 at 1473 K; c) standard powder spectra.

on this substrate (figure 3.22b). Lee and Chun have reported a similar trend in surface morphology change with temperature for the deposition of TiC_x on cemented carbides [108]. They observed, however, a change in preferred orientation from (111) to (110) as the temperature increased from 1273 to 1423 K [144]. Thus, they concluded that changes in preferred orientation are associated with changes in microstructure, with the equiaxed and needle-shaped grains corresponding to (111) and (110) orientation, respectively. Microstructures similar to those shown in figures 3.21a-d have also been reported by Yang et al. on cemented carbides, and Jang and Chun on various steel substrates [107,246].

The morphological evolution of TiC_x coatings on (0001) single crystal Al_2O_3 as the deposition temperature was varied from 1278 to 1383 K is illustrated in figure 3.23. The grain size increased with temperature and the grain shape changed from globular to a faceted structure, presumably caused by an increase in growth rate. A similar trend was observed for the coatings on (1 $\bar{1}$ 02) single crystal Al_2O_3 . The effect of the CH_4 partial pressure on the surface morphology of the films (figure 3.24) was similar to the temperature effect. As expected from the dependence of the growth rate on the CH_4 partial pressure, a significant change in grain size was observed for increasing CH_4 concentrations. The grain shape, however, remained unchanged as the reactant ratio changed. This trend was the same for both Al_2O_3 substrate orientations.

Each film displayed a strong preferred orientation which varied with substrate orientation, deposition time and deposition temperature (table 3.2). For increasing deposition thickness and higher growth temperature, the coatings appeared to be oriented in directions of highest packing. The effect of temperature on preferred orientation is

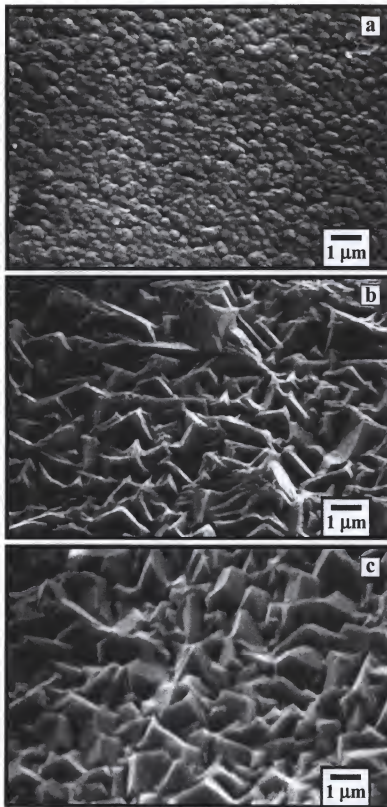


Figure 2.23 Effect of the deposition temperature on the surface morphology of TiC_x deposited on (0001) Al_2O_3 .
a) 1278 K; b) 1313 K; c) 1383 K.

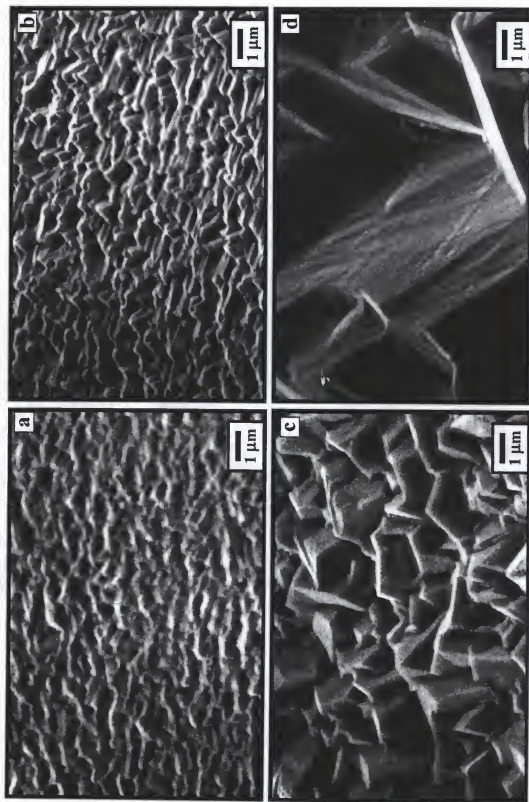


Figure 3.24 Surface morphology of TiC_x films deposited on (0001) Al_2O_3 as a function of the inlet reactant ratio.
 a) $\text{CH}_4/\text{TiCl}_4 = 0.25$; b) $\text{CH}_4/\text{TiCl}_4 = 2$; c) $\text{CH}_4/\text{TiCl}_4 = 0.5$; d) $\text{CH}_4/\text{TiCl}_4 = 4$.

consistent with increasing growth rates, as faster growth occurs on orientations of highest packing. The effect of deposition thickness, on the other hand, is the result of the substrate having less influence over the growth orientation as the deposit extends further away from the interface. The coatings become oriented in directions of highest packing as these orientations are the most dominant in the random XRD pattern. Grain orientations did not, however, vary with CH_4 partial pressure. These results are partially corroborated by Lee and Chun who observed no change in preferred orientation of TiC_x films on cemented carbides with either the reactant concentration, or the deposition time [144]. Conversely, an increase in grain size with increasing deposition temperature and inlet reactant concentration has been reported previously by several authors [107,108,144,154]. Lee and Chun argue that the increase in grain size is due to an enhancement in the nucleation rate in the early stages of growth which also results in a finer grain structure of the films [108]. Nevertheless, Jang and Chun have also shown that the type of substrate plays a major role in determining the effect of reactant concentrations on the grain size of the deposits [107]. They found that for steels with no alloy content (plain carbon steel) the grain size of TiC_x coatings decreased with increasing inlet reactant concentration.

The deposition of TiC_x films on Mo and Ta produced wedge shaped, sharply defined crystallites (figure 3.25). The XRD pattern of TiC_x deposited on Mo at 1423 K (figure 3.26a) shows an enhanced (220) line. The (220)/(200) peak intensity ratio was 7, compared to 0.6 for the random powder pattern (figure 3.26d). At 1473 K, the peak intensity ratio decreased to 0.2 (figure 3.27b), which is opposite to the behavior observed for deposition on graphite. The XRD pattern also shows weak lines representative of

Mo₂C, which presumably formed during the initial stages of deposition. Similar behavior was observed for deposition on Ta substrates where the observed by-product carbide was TaC. XRD revealed a dominant (200) line, suggesting random orientation; except, a strongly enhanced (311) line was also detected (figure 3.26c).

Table 3.2 Preferred orientation of TiC_x films as a function of substrate orientation, deposition time and deposition temperature.

Substrate Orientation: (0001)

Deposition Temperature (K)	Deposition Time (hr)		
	1	2	4
1278	(200)	(200)	(111)
1313	(111)	(111)	(220)
1383	(111)	(111)	(111), (220)

Substrate Orientation: (1 $\bar{1}$ 02)

Deposition Temperature (K)	Deposition Time (hr)		
	1	2	4
1278	(200), (111)	(200), (111)	(111)
1313	(200), (311)	(200), (311)	(200)
1383	(200)	(220)	(220)

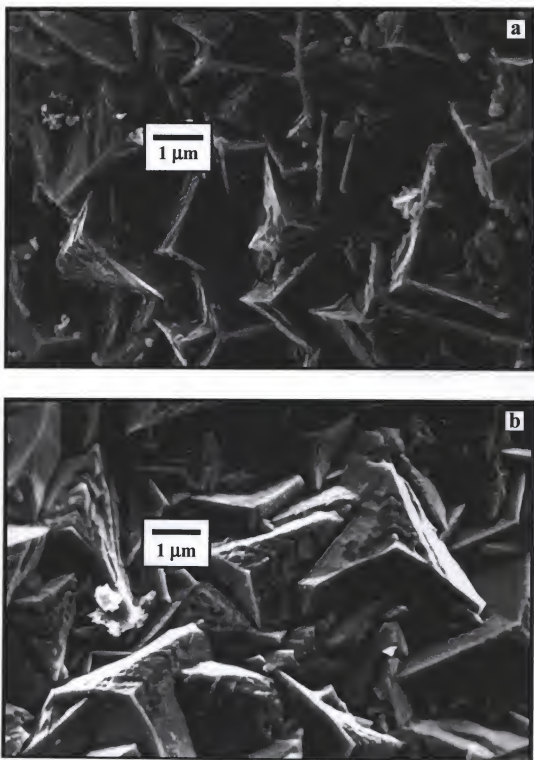


Figure 3.25 Surface morphology of TiC_x deposited at 1423 K on a) Mo; b) Ta.

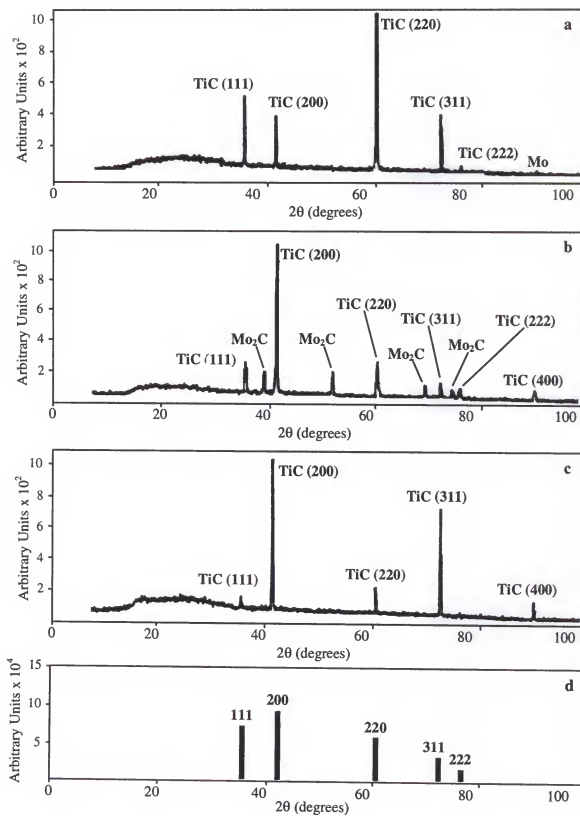


Figure 3.26 XRD patterns of TiC_x films deposited on: a) Mo at 1423 K; b) Mo at 1473 K; c) Ta at 1423 K; d) standard powder pattern.

CHAPTER 4

SINGLE PORE MODEL OF TiC_x CVI

4.1 Introduction

Optimal operation of CVI processes requires maximization of the densification rates as well as the densification uniformity. Because of the complexities stemming from the physical and chemical process complexities, the task of selecting optimal operating conditions is sometimes an empirical one. This has led to the development of a number of predictive models which have evolved from characterizing simple single pore geometries to schemes incorporating complex preform architectures [43,57,147,181-198,247-258]. While the latter versions of these models approach a realistic representation of the process, they provide limited fundamental insight and are cumbersome to manipulate because of their complexity. Furthermore, these models have generally found limited success since they fail to take into account the anisotropic and multimodal nature of the preform porosity.

As a result, several authors have focused their analysis on the simplest geometrical case, namely a single cylindrical pore [41,55,145,193,197,248-250]. The first class of these models were based on treatments similar to that used by Thiele in heterogeneous catalysis, where the reaction rate and concentration profiles are functions of the dimensionless Thiele modulus [41,179]. These approaches assumed first-order heterogeneous kinetics, only Fickian diffusion, and more importantly a time-independent

pore diameter [145]. After this, authors such as Rossignol et al. began incorporating Knudsen diffusion into the analysis, and treated the time variation of the pore diameter by using the quasi-steady state hypothesis [55, 255]. Subsequent work introduced further improvements such as the addition of convection in the mass conservation equations to account for molar changes caused by heterogeneous reactions, reaction orders other than one, and homogeneous gas phase reactions coupled to the heterogeneous process [193,197,248-250].

In this chapter, a single pore model of CVI is introduced. The purpose of the model is not only to provide a guide to design and interpret the experimental plan, but also to test the use of HCl injection to improve current CVI processes. The model is based on a cylindrical geometry. It takes into account forced convection and Fickian and Knudsen diffusion. It can also account for isothermal as well as temperature gradient conditions. The model predicts gaseous concentration profiles, but more importantly the evolution of the deposition profile with time. In particular, the model is the first attempt at simulating the forced-flow, temperature gradient CVI process in a cylindrical pore.

4.2 Model Description

4.2.1 Pore Geometry and Simplifying Assumptions

The geometry employed in the analysis was a straight cylindrical open-ended pore with initial radius R and length L (see figure 4.1). The radial symmetry of the pore allows consideration of only discrete angular sections extending from the center of the pore to the wall. Thus at any point, the deposition cross section is assumed to be a disk. The pore was discretized into n elements in order to take advantage of Graetz-Nusselt's short-

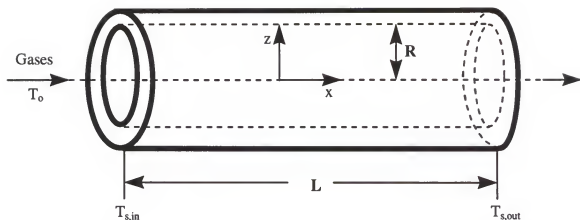


Figure 4.1 Single cylindrical pore geometry used to model FCVI processes.

distance asymptotic solution of the heat and mass transfer equations. In addition, the following assumptions are made: 1) the pore has a large aspect ratio, i.e., $L \gg R$ (typically $L = 1 \text{ mm}$ and $R = 5 \text{ }\mu\text{m}$); 2) the convective flow within the pore is laminar with a linear velocity profile; 3) heat and mass transfer through convection in the radial direction and conduction or diffusion in the axial direction are negligible; 4) no homogeneous reactions occur within the pore; 5) mass transfer processes are rapid compared to changes in the pore diameter (quasi-steady state hypothesis).

The assumption of a linear velocity profile is an approximation that simplifies the solution of the equations of energy and mass conservation. This approximation is fairly accurate for locations near the pore wall. Thus, the assumption is applicable to the model since the deposition rate is limited by the heterogeneous reaction at the wall. Assumption 3 is also justifiable as Peclet number is 3000. The quasi-steady state hypothesis has been analytically justified by Gupte and Tsamopolus [249] who found mass transfer rates to be 100 times faster than the changes in pore diameter.

4.2.2 Momentum and Energy Transfer Equations

By assumption 2, the momentum transfer problem is already defined and the solution is a linear velocity profile, i.e.,

$$V_x(s) = \frac{V_{\max} \cdot s}{R} = \frac{3V_{\text{bulk}} \cdot s}{2R}, \quad (4.1)$$

where $s = R - z$, and $0 \leq s \leq \infty$

With equation 4.1 and the remaining assumptions, the heat and mass transfer equations can be reduced to versions of the short-distance asymptotic Graetz-Nusselt problem [259]. The governing energy transfer equation, after linerization in the z coordinate, is written as

$$V_x \frac{\partial T}{\partial x} = \left(\frac{\kappa}{\rho C_p} \right) \frac{\partial^2 T}{\partial s^2} \quad (4.2)$$

with the following boundary conditions:

$$x = 0, \quad T = T_o \qquad s = 0, \quad T = T_s \qquad s = \infty, \quad T = T_o$$

where T_o is the average gas temperature at the entrance, and T_s is the wall temperature.

By variable substitution, equation 4.2 takes on the dimensionless form:

$$\frac{\partial \Theta}{\partial \lambda} = \frac{1}{\eta} \frac{\partial^2 \Theta}{\partial \eta^2} \quad (4.3)$$

with boundary conditions

$$\lambda = 0, \quad \Theta = 1 \qquad \eta = 0, \quad \Theta = 0 \qquad \eta = \infty, \quad \Theta = 1$$

where $\eta = \frac{s}{R}$; $\lambda = \frac{2x\kappa}{3V_{\text{bulk}}C_p\rho R^2} = \left(\frac{4}{3\text{Pe}_{\text{HT}}} \right) \left(\frac{x}{R} \right)$; $\Theta = \frac{T - T_s}{T_o - T_s}$,

and Pe_{HT} is the heat transfer Peclet number.

The variables η and λ can be transformed into one, yielding a second-order ordinary differential equation in the new variable χ :

$$\frac{\partial^2 \Theta}{\partial \chi^2} + 3\chi^2 \frac{\partial \Theta}{\partial \chi} = 0 \quad (4.4)$$

with

$$\chi = \frac{\eta}{\sqrt[3]{9\lambda}}$$

It becomes clear that the first and third boundary conditions above are similar, and only two are necessary to solve the differential equation, i.e.,

$$\chi = 0, \quad \Theta = 0 \quad \chi = \infty, \quad \Theta = 1$$

The resulting solution is

$$\frac{T - T_s}{T_o - T_s} = 1 - \frac{\int_{\chi}^{\infty} e^{-\beta^3} d\beta}{\int_0^{\infty} e^{-\beta^3} d\beta} \quad (4.5)$$

Since equation 4.5 applies only to a short axial distance inside the pore, it is necessary to discretize the pore into appropriate axial segments, and use the results of equation 4.5 as input conditions for the next segment. In this manner, the temperature profile inside the pore is calculated. It was found that for discrete axial elements (Δx) of 5 μm in length, the difference between the wall temperature and the gas temperature at the axis ($T_s - T[z=0]$) in every element is $\leq 12^\circ\text{C}$. When Δx is increased to 10 μm , $T_s - T[z=0]$ becomes $\leq 1^\circ\text{C}$ in every element. Thus, for discrete axial elements with $\Delta x \geq 10 \mu\text{m}$, $T \approx T_s$. In other words, the gas phase temperature at any radial cross section is constant, and mimics the profile established at the wall. For a linear wall temperature profile, then

$$T = \left(\frac{T_{s,\text{out}} - T_{s,\text{in}}}{L} \right) x + T_{s,\text{out}} \quad (4.6)$$

4.2.3 Mass Transfer and Geometry Change Equations

The mass conservation equations of each of the species are written as

$$V_x \frac{\partial C_i}{\partial x} = D_i \frac{\partial^2 C_i}{\partial s^2} \quad (4.7)$$

with boundary conditions

$$x = 0, \quad C_i = C_i^0 \quad s = 0, \quad D_i \frac{\partial C_i}{\partial s} = v_i R_x \quad s = \infty, \quad C_i = C_i^0,$$

where R_x is the heterogeneous reaction rate expression, and D_i , and v_i are the diffusion and stoichiometric coefficients of each species respectively.

After variable substitution,

$$\frac{\partial \Psi}{\partial \xi} = \frac{1}{\eta} \frac{\partial^2 \Psi}{\partial \eta^2} \quad (4.8)$$

with boundary conditions

$$\xi = 0, \quad \Psi = 1 \quad \eta = 0, \quad \frac{\partial \Psi}{\partial \eta} = \frac{v_i R_x}{D_i C_i^0} \quad \eta = \infty, \quad \Psi = 1$$

where $\eta = \frac{s}{R}$; $\xi = \frac{2x D_i}{3V_{\text{bulk}} R^2} = \left(\frac{4}{3\text{Pe}_{\text{MT}}}\right)\left(\frac{x}{R}\right)$; $\Psi = \frac{C_i}{C_i^0}$,

and Pe_{MT} is the mass transfer Peclet number.

After a similar transformation as in the energy transfer case, the solution is:

$$\frac{C_i}{C_i^0} = 1 + \frac{R^3 \sqrt{9\xi}}{C_i^0 D_i} v_i R_x \int_0^\infty e^{-\beta^3} d\beta \quad (4.9)$$

with

$$\varphi = \frac{\eta}{\sqrt[3]{9\xi}}$$

Equation 4.9 is one of a set of n equations in the n concentration variables. These equations are solved simultaneously at the wall to obtain the heterogeneous reaction rate

term (R_x) in every discrete axial element (determined in section 4.2.2). Once the reaction rate is calculated in a given discrete element, the change in pore diameter due to deposition can be found from the following equation:

$$R_k = R_{k-1} - V_m R_x \Delta t_k \quad (4.10)$$

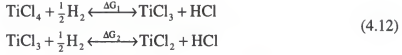
R_k and R_{k-1} are the pore radii at successive time intervals, V_m is the molar volume of the solid deposit, and Δt the time interval. The change in reactant concentrations due to reaction is also calculated, and the result used as input conditions for the next discrete element. The procedure is then repeated for the next element, thus yielding deposition and concentration profiles inside the pore.

4.2.4 Reaction Rate Expression and Diffusion Coefficients

The following rate expression, proposed by Stjernberg et al., was used in the model [162]:

$$R_x = k \frac{C_{CH_4}^{0.5}}{C_{HCl}^{eq,5}} \quad (4.11)$$

Thus, the rate has a first order dependence on the initial concentration of CH_4 at the surface, and is inversely proportional to the surface equilibrium concentration of HCl . This later effect relates the heterogeneous reaction to the homogeneous pseudo-equilibrium between the $TiCl_x$ and HCl species. Consequently, $TiCl_4$ and HCl injection play an implicit role on the rate expression through their influence on the equilibrium amount of HCl . Since $TiCl_4$ and $TiCl_3$ are the two most predominant $TiCl_x$ species, the computation of the equilibrium HCl concentration was performed by considering the following disproportionation reactions:



From these, two equilibrium equations result relating the extents of reaction to the respective Gibbs energies of reaction:

$$\frac{\varepsilon_1 (C_{\text{HCl}}^{0,s} + \varepsilon_1) P^{1/2}}{(C_{\text{TiCl}_4}^{0,s} - \varepsilon_1)(C_{\text{H}_2}^{0,s} - \frac{1}{2}\varepsilon_1)^{1/2}} = e^{\frac{-\Delta G_1^\circ}{RT}} \quad (4.13)$$

$$\frac{-(C_{\text{HCl}}^{0,s} + \varepsilon_1) P^{1/2}}{(C_{\text{H}_2}^{0,s} - \frac{1}{2}\varepsilon_1)^{1/2}} = e^{\frac{-\Delta G_2^\circ}{RT}} \quad (4.14)$$

where $C_{\text{TiCl}_4}^{0,s}$, $C_{\text{HCl}}^{0,s}$ and $C_{\text{H}_2}^{0,s}$ are input surface concentrations, ΔG_1° and ΔG_2° are the Gibbs energies of the reactions, P the total pressure, and ε_1 and ε_2 are the extents of the reactions. For computational purposes, $C_{\text{TiCl}_4}^{0,s}$, $C_{\text{HCl}}^{0,s}$ and $C_{\text{H}_2}^{0,s}$ are taken to be the respective surface concentrations as calculated from the model at the previous x -coordinate discrete element. After simultaneous solution, the equilibrium HCl concentration is calculated from the extents as

$$C_{\text{HCl}}^{\text{eq},s} = C_{\text{HCl}}^{0,s} + \varepsilon_1 + \varepsilon_2 \quad (4.15)$$

The overall diffusion coefficients used in the mass transfer equations are obtained by the combination of Fickian ($D_{i,F}$) and Knudsen ($D_{i,K}$) diffusion coefficients according to Bosanquet's definition

$$\frac{1}{D_i} = \frac{1}{D_{i,F}} + \frac{1}{D_{i,K}} \quad (4.16)$$

with $D_{i,F} = \Phi_{i,F} \frac{T^{3/2}}{P}$, and $D_{i,K} = \Phi_{i,K} RT^{1/2}$,

where $\Phi_{i,F}$ and $\Phi_{i,K}$ are coefficients dependent on material properties. Because the

reactants are present in dilute concentrations, the diffusion coefficients are assumed to be concentration independent. To calculate the Knudsen diffusion coefficient at a given time interval (Δt_k) and axial position x , the pore radius from the previous time interval (Δt_{k-1}) at the given axial position is used. Consequently, since the Knudsen diffusion coefficient is a linear function of the pore radius, it is important to select sufficiently small discrete time intervals so that the pseudo-steady state assumption remains valid during the calculation procedure. Typical TiC_x CVD growth rates are 0.001 to 0.002 $\mu\text{m/s}$. Since CVI growth rates are even slower, pore diameter changes with $\Delta t=1$ sec. are negligible compared to the initial pore diameter (10 μm). Thus, $\Delta t=1$ sec. was used to obtain the results in section 4.3. Table 4.1 contains a list of constitutive constant values at 900 and 1200 $^\circ\text{C}$ which are typical inlet and outlet temperatures used in temperature-gradient CVI.

4.2.5 Calculation Method

Since the model required the discretization of the axial distance coordinate as well as the time coordinate, all the model computations were performed with the aid of a FORTRAN program. A listing of the program source code, GNM3, can be found in appendix 2. The calculation procedure consisted of the following steps:

- 1) Starting at the initial time (t_0), the pore radius is fixed at its initial value (R_0) for all the discrete elements in the x coordinate. At every element, the temperature is calculated as the arithmetic mean of the corresponding temperature bounds given by a linear profile if a temperature gradient is applied to the pore wall.
- 2) From the temperature and pore radius, the reaction rate constant, diffusion coefficients, and equilibrium concentration of HCl are computed.

3) The mass transfer equations are solved simultaneously at the wall to obtain the reaction rate at the given discrete element. From the resulting deposition rate, the change in pore radius for the discrete element is calculated. For the first discrete element, the reactant concentrations at the pore entrance are used as input conditions, while for every element thereafter, the concentrations at the wall from the previous element are used as input conditions.

4) The concentration profiles of all the gaseous species are calculated within the element using the mass transfer equations.

5) Iteration is made to the next element and steps 2 to 4 are repeated.

6) Once the calculation is completed along the length of the pore, iteration is made in the time coordinate, and steps 2 to 5 are repeated.

4.3 Results and Discussion

To determine the ability of the model to predict general trends in the deposition rate and uniformity, various infiltration conditions were considered. As an example, figure 4.2 shows the results of a model simulation at a constant wall temperature of 1200 °C and 500 Torr for a pore length and diameter of 1 mm and 10 μm , respectively. The distance along the pore axis and successive deposition profiles were normalized with respect to the pore length (L) and the pore radius (R). Thus, whenever a deposition profile reaches a value of 1 on the normalized deposition thickness axis, the pore becomes "pinched" or sealed at that particular location, and densification stops for areas of the pore at higher normalized pore length values. It is evident that at the above conditions, the

densification process produces a non-uniform deposit with the pore becoming pinched at the entrance, and a relatively large amount of residual porosity remaining.

It is well known that reduced infiltration temperature and pressure, while leading to lower infiltration rates, result in more uniform densification. Figure 4.3 shows deposition profiles resulting for an infiltration temperature of 900 °C and a pressure of 100 Torr. Clearly, the infiltration rate is lower, but the deposit has a greater degree of uniformity. The potential “pinch” point, however, remains at the entrance.

Similar improvement is expected by the use of a temperature gradient. Figure 4.4 illustrates this effect when a temperature difference of 900-1200 °C is applied between the inlet and outlet. In this case, the enhancement in the infiltration uniformity is more pronounced than the previous case even though the pressure remained at a value of 500 Torr. More importantly, the eventual point of closure is observed to shift to the interior of the pore.

The primary objective of this model was to determine the influence of HCl injection, in conjunction with a temperature gradient, on the infiltration uniformity. In this case, the “pinch” point location is determined by the relative importance of the temperature gradient (higher deposition rate at higher temperature) and HCl production (lower deposition rate at higher HCl concentration) modulated by the inlet HCl. Figure 4.5 shows, the evolution of the deposition profile when the temperature difference is 900 to 1200 °C and HCl is injected at a concentration of 2.5 mole %. As expected, the rate is observed to decrease since the added HCl reduces the rate of heterogeneous reaction (see equation 4.11). The deposition uniformity is seen to increase over each of the previous cases. As the concentration of HCl is increased to 5 mole % (figure 4.6) and 10 mole %

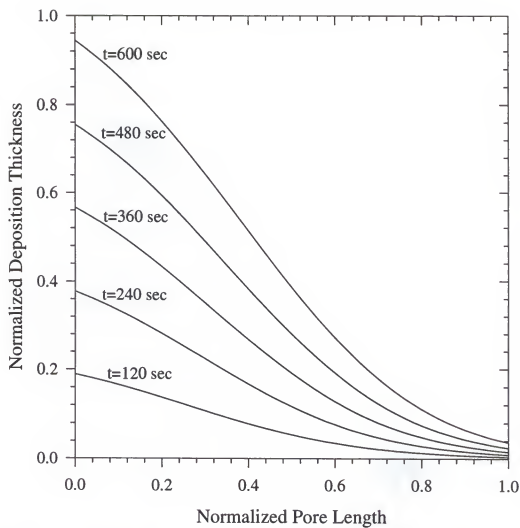


Figure 4.2. Deposition profiles predicted by the single pore model ($T=1200^{\circ}\text{C}$, $P=500$ Torr).

(figure 4.7), the potential "pinching" point is seen to travel further inside the pore until eventually is located at the pore outlet. Thus, according to the model results, it is possible to densify the pore from outlet to inlet, without leaving isolated porosity behind, by choosing a suitable temperature gradient and inlet HCl concentration. It is also reasonable to assume that this process can be extended to more complex preform geometries to reduce density gradients in the resulting composites.

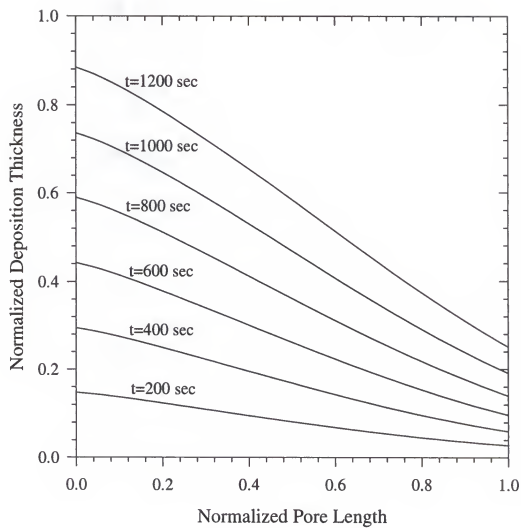


Figure 4.3. Deposition profiles predicted by the single pore model ($T=900^{\circ}\text{C}$, $P=100$ Torr).

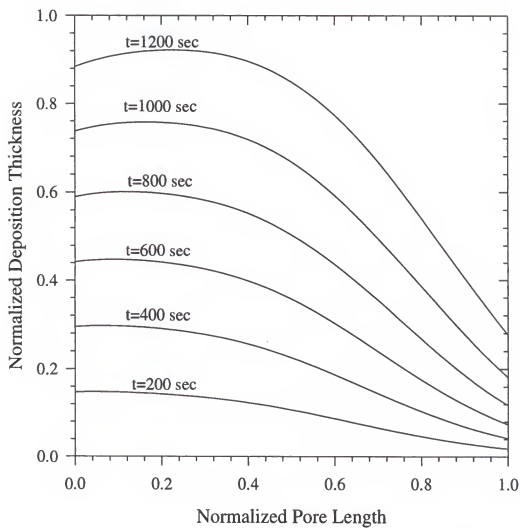


Figure 4.4. Deposition profiles predicted by the single pore model (Temperature gradient = 900 - 1200 °C, $P=500$ Torr).

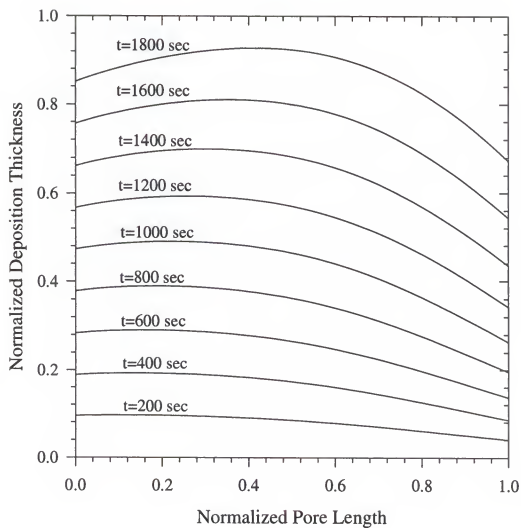


Figure 4.5. Deposition profiles predicted by the single pore model (Temperature gradient = 900 - 1200 °C, $P = 500$ Torr, HCl concentration = 2.5 %).

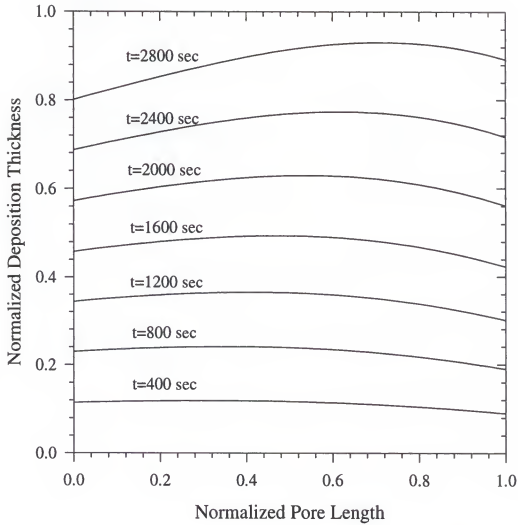


Figure 4.6. Deposition profiles predicted by the single pore model (Temperature gradient = 900 - 1200 °C, $P = 500$ Torr, HCl concentration = 7.5 %).

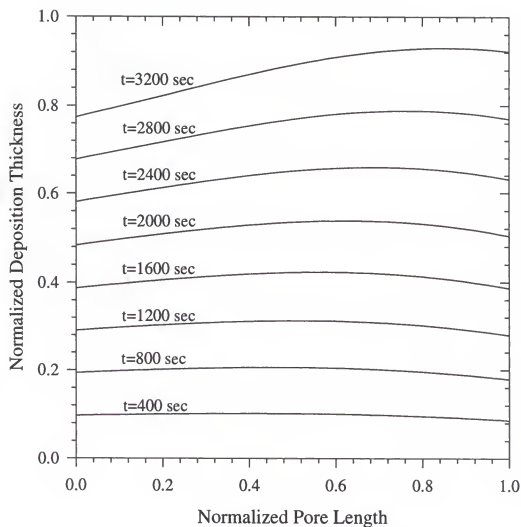


Figure 4.7. Deposition profiles predicted by the single pore model (Temperature gradient = 900 - 1200 °C, $P = 500$ Torr, HCl concentration = 10 %).

CHAPTER 5

CVI OF NICALON PREFORMS WITH TiC_x

5.1 Introduction

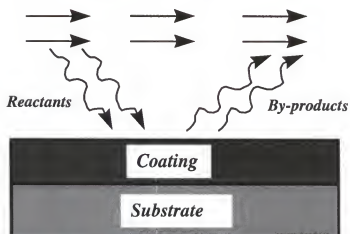
The mechanical properties of ceramic composite materials depend on the individual properties of the matrix and reinforcing phase, and to their interfacial properties. Therefore, the fabrication process plays a major role in the ultimate composite properties by the way that it alters the properties of the individual components and the characteristics of the interface. Conventional techniques such as hot pressing subject reinforcing fibers to deleteriously high temperatures and pressures. For instance, SiC-based Nicalon fibers are reported to degrade at temperatures above 1000 °C which is below the temperature required to sinter SiC [260]. These fibers are also susceptible to the mechanical stresses required in high-pressure consolidation techniques. The need to protect the composite elements from damage and to improve interface dependent properties such as fracture toughness has motivated the development of a new class of vapor-phase synthesis techniques termed chemical vapor infiltration (CVI). CVI not only allows composite fabrication at relatively lower temperature and pressure than hot pressing techniques, but also the use of gaseous precursors results in better control of the interfacial properties than attainable from liquid routes such as polymer impregnation [260].

Descriptively, CVI is a derivative of CVD, differing from the latter in that deposition occurs both on the outside surfaces of the substrate and inside its pore network [5]. Thus, by this method, composites are fabricated by densification of the porous structure of a whisker or continuous fiber array (reinforcing phase) with the depositing coating (matrix phase) [30]. Figure 5.1 schematically compares examples of simple CVD and CVI processes, and illustrates processing characteristics which lead to inadequate preform densification due to premature pore closure. In contrast to CVD, it is desirable to operate CVI kinetically controlled conditions, i.e., transport of the reactants throughout the pore, neglecting reactant depletion effects, is faster than the heterogeneous deposition reactions at the pore wall [11]. As a result, sufficient time is allowed for reactants to reach the end of the pore before they are depleted, thus producing a uniform deposit thickness across the length of the pore. Otherwise, reactants are consumed primarily at the pore entrance, causing pore "necking", and eventually sealing the pore from further densification.

CVI processes are generally classified into five categories which are illustrated in figure 5.2 [36]. Industrially, isobaric-isothermal CVI (ICVI) is the most widely used type of these processes and the first developed (type I, figure 5.2) [30]. Because ICVI relies solely on diffusion to transport the reactants into the preform, ICVI processes are normally operated at relatively low temperature and pressure, conditions which enhance transport while slowing the rate of deposition reactions. Consequently, ICVI is a notoriously slow densification process, requiring from weeks to months to complete [1].

To improve on this issue, other variations of CVI have been used to accelerate the densification rate without resulting into unacceptable residual porosity from premature

Chemical Vapor Deposition



Chemical Vapor Infiltration

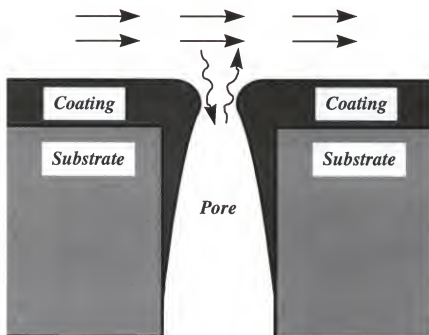


Figure 5.1 Comparison of CVD and CVI processes.

pore closure. The most promising of these techniques is forced-flow temperature-gradient CVI (FCVI), developed at ORNL [59]. In this process, simultaneous and diametrical temperature and pressure gradients are applied across the preform (type IV, figure 5.2). The convective flows resulting from the pressure gradient provide an ample supply of reactants to all parts of the preform, speeding deposition of the matrix. At the same time, the temperature gradient assures maximum deposition at the outlet side of the preform first, thus keeping the colder areas of the preform accessible to further infiltration. As complete densification is approached at the hottest side of the preform, the thermal conductivity of the developing composite increases which transfers additional thermal energy to neighboring areas. Thus, infiltration is accelerated in these regions. The overall infiltration process can be visualized as an advancing reaction front, densifying the preform from the hot to cold side [30,76]. FCVI reduces processing times to tens of hours without producing significant density gradients in the final composite [1]. Still, FCVI use is limited to preforms with simple geometry, as special and dedicated equipment is necessary to apply the temperature and pressure gradients [258].

In this chapter, a new CVI process is introduced which provides additional refinements to the traditional FCVI process. At the center is the issue of infiltration control flexibility. Once established, the temperature gradient and other processing parameters in FCVI evolve naturally as densification proceeds, outside the reach of the operator. The addition of HCl to a chloride reactant chemistry provides one more parameter which can be used in tandem with the temperature gradient to achieve better control over the infiltration process. An advantage of such an approach is the ability to reverse the process to the point where infiltration can be completely stopped in regions of

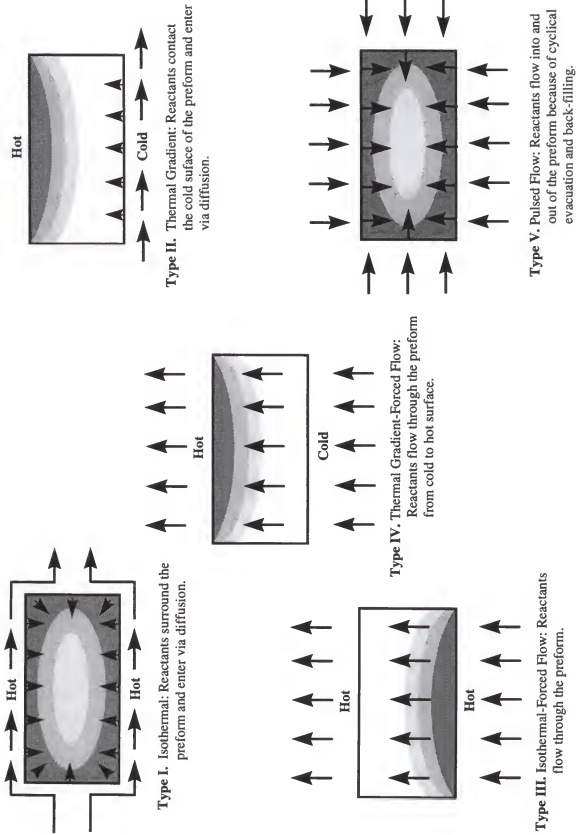


Figure 5.2 General classifications of CVI processes [36].

the preform while it proceeds in others. The process of FCVI coupled with HCl injection is thus presented in the following sections. Nicalon preforms and TiC_x were used as reinforcing and matrix materials, respectively. The fabrication of TiC_x -Nicalon composites by type II CVI will be discussed first. This will be followed by a study of the FCVI of the same composites. Finally, the process of FCVI with HCl injection is investigated.

5.2 Theoretical Description

A justification, based on equilibrium analysis, for the process of temperature gradient CVI coupled with HCl injection was established in chapter 2. By thermodynamic modeling, it was demonstrated that an deposition-etch boundary exists defining operational zones where deposition or no deposition of TiC_x occur (see figure 2.20). It was shown that this boundary is a function of the deposition temperature and added HCl concentration, and that the deposition zone lies in the region of high deposition temperature and low HCl concentration. Further justification was given in chapter 4, where a single pore geometry was used to model CVI processes. The model demonstrated that temperature-gradient CVI coupled with HCl injection results in a greater composite density than attainable with temperature-gradient CVI alone.

On this basis, a CVI process was devised that takes advantage of these features to improve the infiltration efficiency and control. This process is illustrated in figure 5.3 where a preform schematic has been superimposed on figure 2.20 representing the etch-deposition boundary. Although not correct, a linear temperature gradient is assumed on the preform for simplicity. This gives a linear correspondence between the temperature

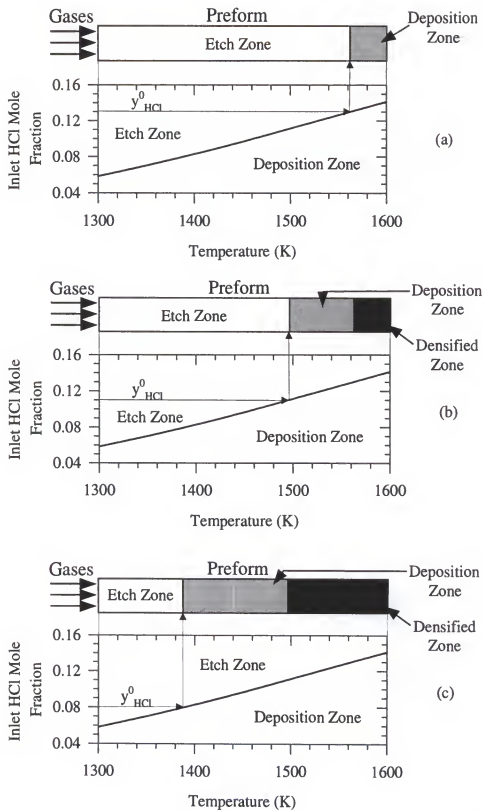


Figure 5.3 Illustration of temperature gradient CVD combined with HCl injection.
 a) $y_{\text{HCl}}^0 = 0.13$; b) $y_{\text{HCl}}^0 = 0.11$; c) $y_{\text{HCl}}^0 = 0.08$.

scale on the graph and the distance along the preform. At the outset of operation, a temperature gradient is first imposed onto the preform, and HCl is injected at a concentration level such that the entire preform lies within the etching zone. Densification is initiated then by lowering the HCl concentration so that a fraction of the preform in the highest temperature regime lies in the deposition zone (figure 5.3a). After densification reaches a sufficient level within this section, the HCl concentration is further reduced to allow deposition in the colder regions (figure 5.3b). The process continues until densification is achieved throughout the preform (figure 5.3c). It is important to note that the increase in thermal conductivity with densification increases the temperature gradient in the nondensified region, thus producing a naturally progressing densification process. Consequently, the reductions in the HCl inlet concentration, necessary to allow the reaction plane to advance along the entire preform, are expected to be lower. Obviously, the greatest advantage of such a scheme is the fact that infiltration can be extinguished at any point in the preform by sufficiently raising the HCl concentration, thus improving control over the densification in progress.

5.3 Experimental Apparatus and Procedure

The experimental apparatus described in chapter 3 was also used to perform the CVI experiments. Modification of the susceptor geometry was, however, necessary to handle the fiber preform substrates. For the initial series of experiments, which were of the type II CVI category, the susceptor-holder set-up depicted in figure 5.4 was used. Gas flow through the annulus between the susceptor and the quartz reactor wall was prevented using a graphite felt plug in order to concentrate the gases around the area of the preform.

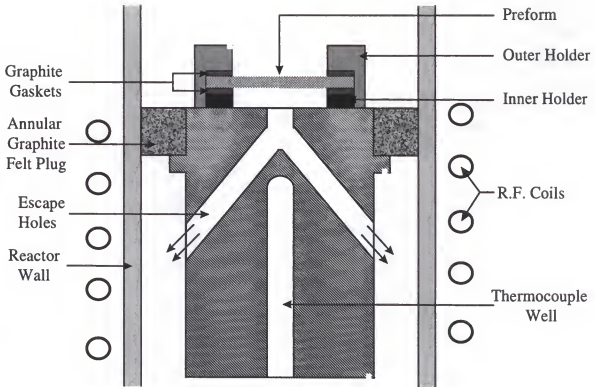


Figure 5.4 Schematic of type II CVD holder-susceptor set-up.

Nonetheless, isobaric conditions were maintained by providing escape passages for the gas through the susceptor. Since the preform was heated only from the bottom by direct radiation from the susceptor, an initial temperature gradient of approximately 300 °C was measured across the preform. The temperature gradients were obtained by taking the difference of the temperatures measured by a pyrometer focused on the top preform surface and the temperature measured by a thermocouple placed inside the susceptor. It was assumed that the latter temperature was the same as that at the bottom preform surface.

For the FCVD process, the injector-holder arrangement shown in figure 5.5 was used. In this set-up, the flow path through the preform was sealed with grafoil gaskets compressed by the injector and holder cup. Radial escape holes were also provided in the

holder cup so that gases could flow out after the bottom preform layers were fully densified. The temperature gradient was once again provided by heating only the bottom with direct radiation from the susceptor, and by virtue of keeping the holder cup outside the r.f. field. The initial gradient was obtained in the same manner as in the ICVI experiments. In both types of experiments, the preforms were stacks of three one-inch disks of 12 harness satin Nicalon fiber weave obtained from Dow Corning. Nicalon fibers are based on a Si-C-O chemistry. The oxygen in the fibers originates from precursors used in the cross linking step of the manufacturing process. The oxide chemistry is the reason why Nicalon degrades rapidly at high temperature and why it develops strong interfaces (poor interfacial properties) in SiC/Nicalon composites. The fibers in the weaves used had an average diameter of 10 μm . When staking the disks, each was oriented so as to continue the weave pattern of the adjacent disk above or below.

After introducing the holder with the preform into the reactor, the chamber was evacuated and purged with Ar as was described in section 3.3. Then, the pressure was stabilized with a H_2 stream to a setpoint below atmosphere (normally 500 Torr), followed by heating of the susceptor to the chosen temperature set-point. After holding at these conditions for 10 min., the infiltration was started by introducing the precursors into the reactor. Type II infiltrations were carried out for various amounts of time, the longest lasting 36 hrs. The length FCVI experiments, on the other hand, was determined by the time necessary for the initial reactor pressure to rise to atmospheric pressure. The duration of these experiments typically varied from 8 to 15 hrs., and in cases when an infiltration time longer than 15 hrs. was foreseen, the experiment was stopped at 15 hours.

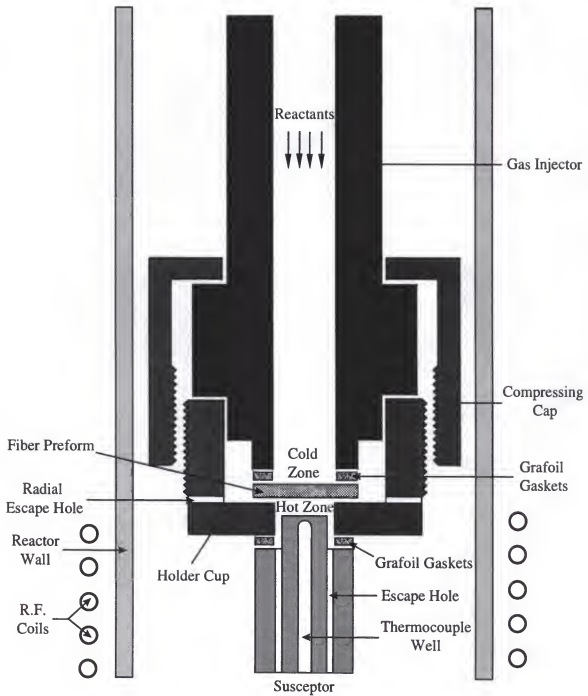


Figure 5.5 Schematic of the injector-holder-susceptor set-up used for FCVI experiments.

After infiltration, the resulting composite was cast in acrylic or epoxide mounts, cut into cross sections, and polished down to 0.25 μm grid. The overall densification rate was determined by ex-situ weight measurements before and after processing. Furthermore, to quantify the densification uniformity, a point-counting statistical technique was applied to SEM micrographs of the composite cross section. These measurements yielded volume fractions of fibers, matrix and residual porosity after processing.

5.4 Results and Discussion

As mentioned before, the initial temperature gradient in the type II CVI experiments was 300 °C (1000 to 1300 °C). The reactor pressure and total flow rate were 1 atm. And 500 sccm, respectively. In addition, the reactant flow rates were 20 sccm for CH_4 and 5 sccm for TiCl_4 . The majority of samples infiltrated using type II CVI did not display significant densification after a standard processing time of 12 hrs. There was little or no bonding between the weave disks, and the fiber bundles within the disks disintegrated upon handling. As a result, an infiltration experiment was carried out for a 36 hour period to gauge the feasibility of type II CVI in further runs. SEM cross sections of this sample are shown in figure 5.6. The effect of the temperature gradient is evident as most of the matrix deposition occurred in the lower disk. Although densification was obtained to permit SEM analysis, the weave disks once again failed to bond with each other, indicating that longer infiltration times would be required. Since the experimental apparatus lacked the safety systems necessary for extended unattended operation, longer deposition times could not be tested.

A type IV CVI approach is expected to increase the deposition rate. Cross sections of a similar preform sample infiltrated by type IV CVI is shown in figure 5.7. Again, the initial temperature gradient was 300 °C with a cold zone temperature of 1000 °C (top surface of the uppermost disk) and a hot zone temperature of 1300 °C (bottom surface of the lowermost disk). The reactant flowrates were 40 sccm of CH₄ and 5 sccm of TiCl₄ in a balance of H₂ to give a total flowrate of 500 sccm.

At the outset of the experiment, the initial reactor pressure was 500 Torr. From the beginning of the experiments, pressure oscillations were observed. The fluctuations always had a maximum of 500 Torr (set-point); however, the minimum pressure readings varied, dropping further and further below the set-point as infiltration proceeded. The period of oscillation varied becoming longer as the magnitude of the oscillations increased. The largest oscillations had a cycle time as long as 30 sec. After 4 hours, the oscillation minimum reached its lowest value of 300 Torr. From this point on, the minimum increased until the oscillations disappeared at 7 hours into the experiment. Following this, the pressure increased monotonically until reaching atmospheric pressure after 9.33 hours at which time the process was stopped. The variation of the average reactor pressure with infiltration time is shown in figure 5.8. A similar behavior of the reactor pressure was observed in all other type IV CVI experiments.

The pressure oscillations are attributed to changes in the flow conductance caused by the densification of the preform. Initially, the decrease in the effective cross-sectional area for flow through the preform led to an increase in the gas velocity which caused the undershoot of the pressure set-point. Eventually, the decrease in conductance became a flow obstruction, causing the pressure to rise monotonically.

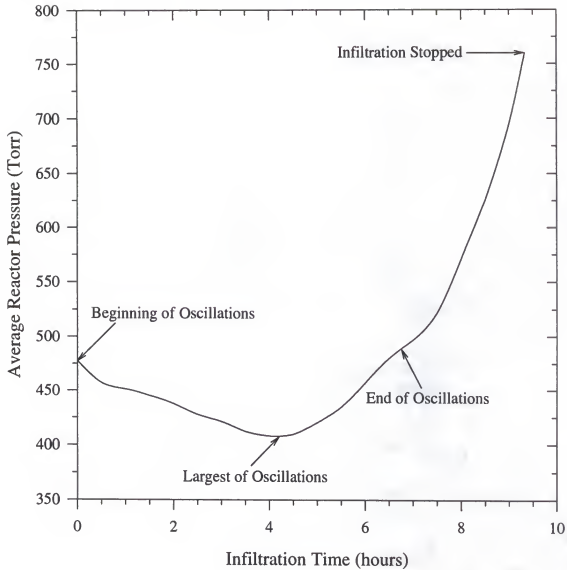


Figure 5.8 Variation of the reactor pressure during infiltration. $P_{\text{CH}_4}^0 / P_{\text{TiCl}_4}^0 = 8$, $F_i = 500$ sccm, $P_i = 500$ Torr, initial temperature gradient = 300°C .

During infiltration, the power supplied to the susceptor was increased to maintain the hot zone temperature constant. This is necessary because as the preform densifies, its thermal conductivity increases. As a result, heat transfer from the denser zones (hotter zones) increases and thus, more power is required to maintain a given temperature. The cold zone temperature, on the other hand, increased monotonically as the matrix

deposition improved the heat transfer properties of the preform. This resulted in a steady decrease of the overall temperature gradient during the majority of the infiltration and was evidence that deposition was progressing gradually from the outlet side to the inlet side of the preform (see figure 5.9). The time where the temperature gradient is seen to temporarily increase coincides exactly with the end of the pressure oscillations and monotonic rise of the reactor pressure. This effect can be explained by a drop in the cold zone temperature because of enhanced heat transfer to the gas phase as the gas density increases. Several factors, such as a higher thermal conductivity at higher pressure, increased convection or increased scattering of radiant heat at higher density, could account for the lower temperature.

On a qualitative basis, SEM analysis indicates that under similar conditions the use of convective transport of the reactants increases the densification rate. Furthermore, the temperature gradient is shown to have the expected effect as evidenced by the greater matrix densities seen in the lower regions of the preform. This set of processing conditions yielded an overall deposition rate of 135 mg/hr of matrix material. A densification rate in terms of volume percent was not calculated as the initial porosity of the preform was unknown. Although extreme care was used in casting the cross sectional samples, trapped volumes of residual porosity acted as defect centers from which sections of matrix and fibers broke off and pulled out during the cutting and polishing procedures (see figure 5.7). This made it difficult to determine the true fraction of residual porosity after infiltration.

A similar infiltration was performed using a lower flowrate of CH_4 (20 sccm) while holding the flowrate of TiCl_4 at the same value as in the previous experiment

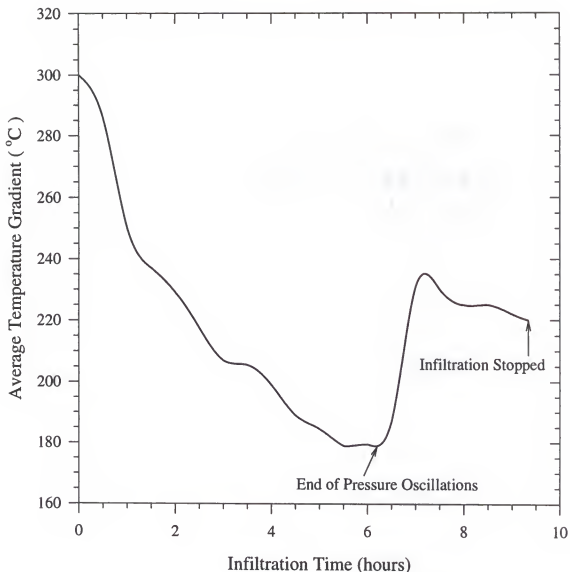


Figure 5.9 Changes in the preform temperature gradient during infiltration. $P_{\text{CH}_4}^0 / P_{\text{TiCl}_4}^0 = 4$, $F_i = 500$ sccm, $P_i = 500$ Torr, initial temperature gradient = 300°C .

(5 sccm). The infiltration process was stopped after 9.33 hours as in the previous run; nevertheless, the average reactor pressure reached only 417 Torr. The densification rate in this case was 114 mg/hr. The lower degree of densification (see figure 5.10) is consistent with the lower reaction rate at low CH_4 concentration, as discussed in chapter 3. Both the lower reactor pressure and reduced infiltration level are indications that despite the

transport limitations imposed by the preform the infiltration process is still affected by kinetic parameters. Also, as anticipated, reducing the densification rate extends the length of the infiltration process (evidenced by the lower reactor pressure) which should lead to less trapped residual porosity. It is recognized that these comparisons can only be made on a qualitative basis since the criterion for termination of the process was a time basis and not the pressure level in the reactor.

Table 5.1 summarizes the effect of the various infiltration parameters on the densification rate and ultimate reactor pressure level. The average pressure was the mean of the maximum and minimum pressure at a given time. The symbols ($\downarrow$) and ($\uparrow$) indicate whether the final pressure was dropping toward or rising from the pressure minimum, respectively. A constant infiltration time of 9.33 hours was used in all experiments. Because the criteria for stopping the infiltrations was a constant time, different final average pressures resulted as the amount of densification reached different levels under different operating conditions. Plots of the densification rate versus these parameters are presented in figures 5.11-13. The reactant ratio was varied by changing the concentration of CH_4 while holding the concentration of TiCl_4 constant at 1 mole %. Thus, in effect, the variation of the densification rate observed in figure 5.11 is due to changes in the CH_4 concentration. The slope of the linear regression through the data indicates a significant departure from the kinetic behavior discussed in chapter 3. The rate is also seen to increase monotonically with both the total mass flow rate and the initial reactor pressure which is expected as more reactant material is available for reaction. At the high flow rate value, however, the rate decreased. This effect can be attributed to a shift to a kinetically

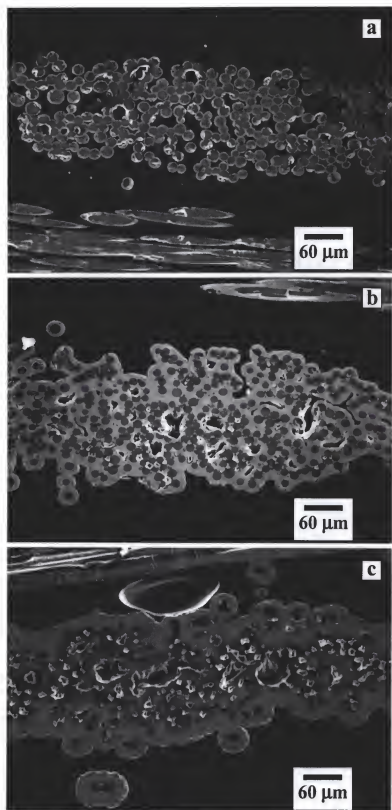


Figure 5.10 Forced-Flow Temperature Gradient CVI ($\text{CH}_4/\text{TiCl}_4 = 4$).
a) Inlet Weave Disk; b) Middle Weave Disk; c) Outlet Weave Disk.

Table 5.1 Summary of infiltration conditions and resulting densification rates.

$$y_{\text{TiCl}_4}^0 = 0.01, t = 9.33 \text{ hrs.}, T_{\text{hot}} = 1300^\circ\text{C}.$$

Reactant ratio (CH ₄ /TiCl ₄)	Total Flow Rate (sccm)	Initial Reactor Pressure (Torr)	Overall Desification Rate (mg/hr)	Average Final Reactor Pressure (Torr)
8	500	500	135	760 (↑)
4	500	500	114	417 (↑)
2	500	500	95	426 (↓)
1	500	500	86	464 (↓)
1	250	500	81	474 (↓)
1	750	500	103	480 (↑)
1	1000	500	90	431 (↓)
1	250	400	72	381 (↓)
1	250	300	60	279 (↓)
1	250	200	57	182 (↓)

controlled mode of deposition and to the ensuing decrease in reactants residence time as the gas phase velocity increases.

Since the primary objective of this investigation was to assess the effect of HCl addition, several experiments were performed at various concentrations and concentration schedules of HCl. A standard set of all other operating parameters was then established with reactant flow rates of 40 sccm of CH₄ and 5 sccm of TiCl₄, and a total flow rate of 500 sccm. An initial temperature gradient of 300 °C, as previously described, was set across the preform, and an initial reactor pressure setpoint of 500 Torr was chosen. All

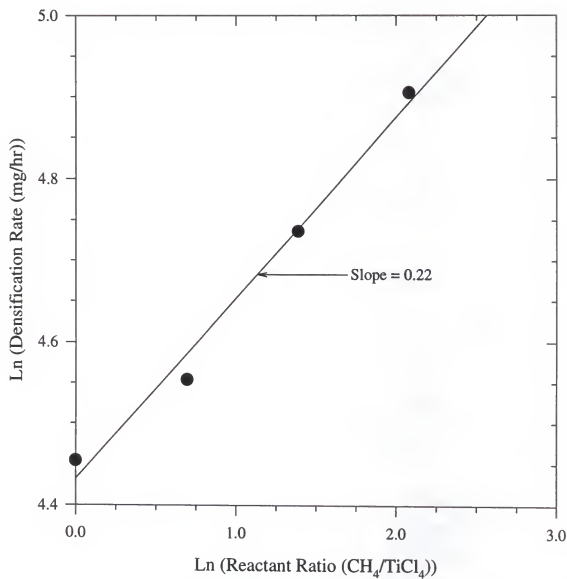


Figure 5.11 Variation of the densification rate with the reactant ratio, ($y^0_{\text{TiCl}_4} = 0.01$).

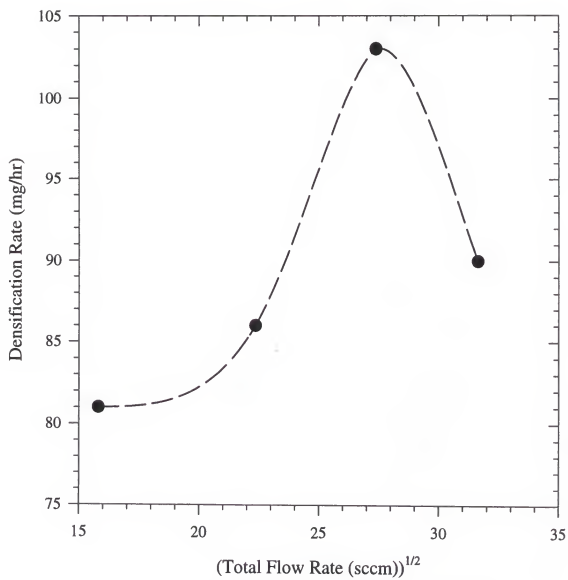


Figure 5.12 Effect of the total flow rate on the densification rate.

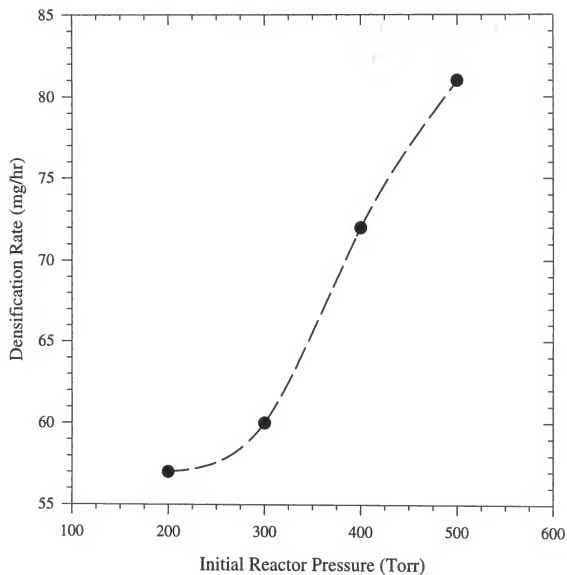


Figure 5.13 Variation of the densification rate with the initial reactor pressure.

experiments were stopped after the reactor pressure reached 760 Torr regardless of infiltration time. A high reactant ratio ($\text{CH}_4/\text{TiCl}_4 = 8$) was used to speed up the densification rate since longer infiltration times were expected with added HCl.

The first set of experiments examined the effect of increasing flowrates of injected HCl on the densification rate and infiltration efficiency (fraction of residual porosity). The volume fractions of deposited matrix and residual porosity were inferred from a statistical point count of cross sectional SEM images of the composites. A total of two thousand points were considered per area ($500\text{ }\mu\text{m} \times 500\text{ }\mu\text{m}$) examined. The densification rate was then calculated as the fractional decrease in porosity over the infiltration time. Table 5.2 summarizes the results of this analysis while cross sectional SEM micrographs of the resulting composites are shown in figures 5.14-17. The fraction of infiltrated initial porosity was defined as the residual porosity divided by the total initial porosity (i.e., the fraction of residual porosity added to the fraction of deposited matrix). The densification rate was simply the fraction of infiltrated initial porosity divided by the overall infiltration time.

From the results presented in table 5.2, it is evident that as the HCl concentration increases the overall fraction of residual porosity left in the sample steadily decreases. Moreover, when HCl is not injected, a porosity gradient results with the greater porosity fractions occurring in the upper layer. As more HCl is injected, this gradient decreases, indicating an improvement in infiltration uniformity. A similar conclusion can be drawn from the fraction of initial porosity ultimately infiltrated. With more HCl, an increasing percentage of the initial porosity is densified at the end of the process. In addition, the amount of densification becomes more uniform across the different layers. A parallel

Table 5.2 Infiltration efficiencies and densification rates resulting from thermal gradient C'VI with constant HCl injection.

Mole % of inlet HCl	Overall Infiltration Time (hr)	Analysis Area	Percentage of Deposited Matrix (TiC _x)	Percentage of Residual Porosity	Percentage of Infiltrated Initial Porosity	Densification Rate (hr ⁻¹)
0	8.67	Top Layer	31.5	9.9	76.0	8.8
		Middle Layer	35.0	10.9	76.2	8.8
		Bottom Layer	32.9	21.8	60.1	6.9
		Overall Sample	33.1	14.2	70.8	8.2
0.1	9.75	Top Layer	36.8	17.6	67.6	6.9
		Middle Layer	43.4	13.8	75.8	7.8
		Bottom Layer	41.4	11.5	78.3	8.0
		Overall Sample	40.5	14.3	73.9	7.6
0.5	12.25	Top Layer	26.9	10.5	71.9	5.9
		Middle Layer	42.3	6.9	85.9	7.0
		Bottom Layer	44.4	11.4	79.6	6.5
		Overall Sample	37.9	9.6	79.1	6.5
1.0	13.25	Top Layer	43.6	8.1	84.3	6.4
		Middle Layer	49.5	8.5	85.4	6.4
		Bottom Layer	60.9	6.8	89.9	6.8
		Overall Sample	51.3	7.8	86.5	6.5

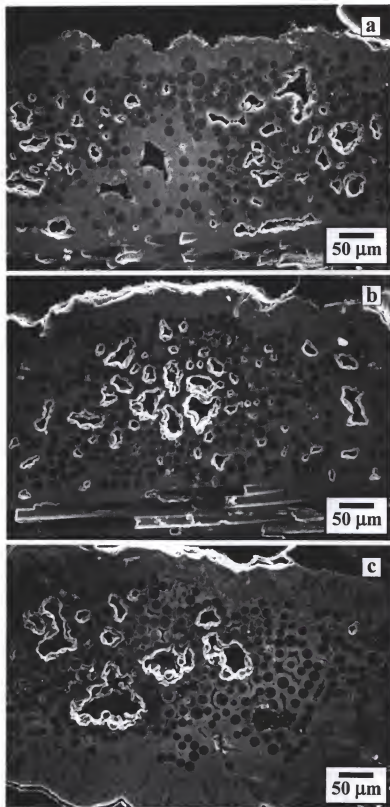


Figure 5.14 Forced-Flow Temperature Gradient CVI without HCl Injection.
a) Inlet Weave Disk; b) Middle Weave Disk; c) Outlet Weave Disk.

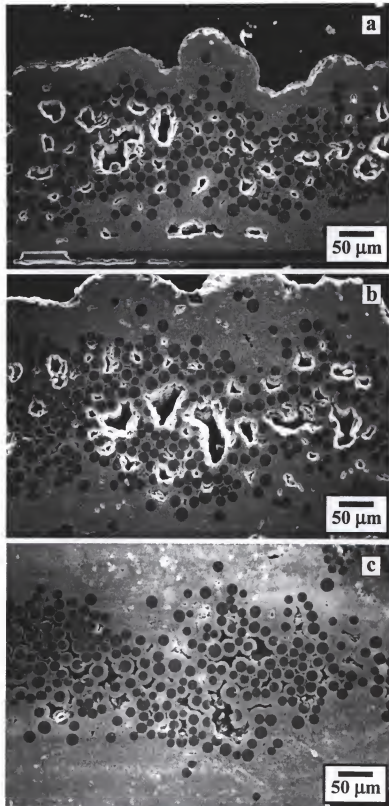


Figure 5.15 Forced-Flow Temperature Gradient CVI with HCl Injection ($y_{\text{HCl}}^0 = 0.1\%$).
a) Inlet Weave Disk; b) Middle Weave Disk; c) Outlet Weave Disk.

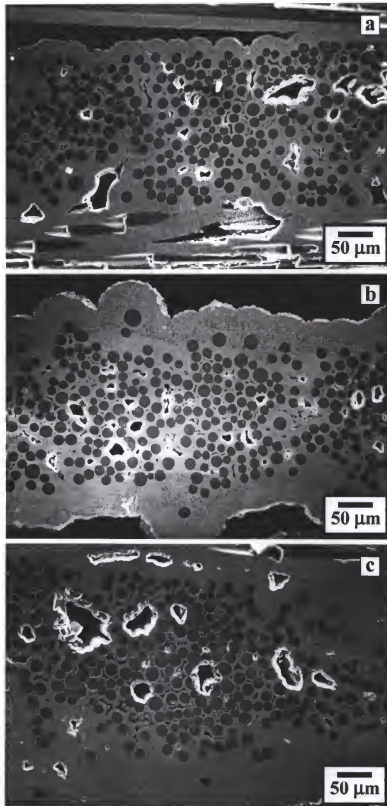


Figure 5.16 Forced-Flow Temperature Gradient CVI with HCl Injection ($y_{\text{HCl}}^0 = 0.5\%$).
a) Inlet Weave Disk; b) Middle Weave Disk; c) Outlet Weave Disk.

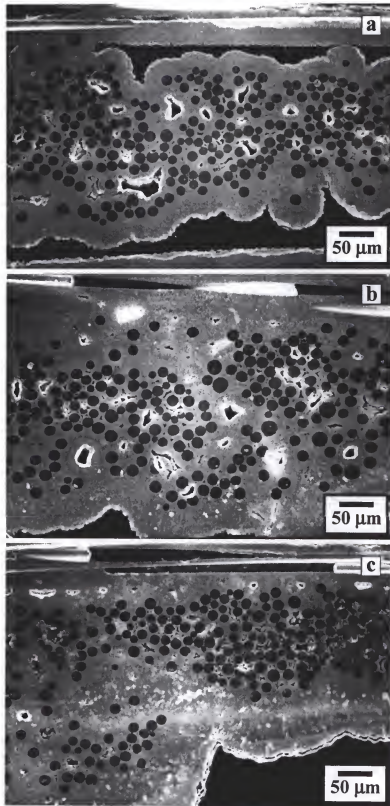


Figure 5.17 Forced-Flow Temperature Gradient CVI with HCl Injection ($y_{\text{HCl}}^0 = 1\%$).
a) Inlet Weave Disk; b) Middle Weave Disk; c) Outlet Weave Disk.

behavior is seen with the fraction of deposited matrix. As more porosity becomes accessible to densification, more material is ultimately deposited. On the other hand, an opposite trend is observed with respect to the densification rate. Although, HCl addition produces a more efficient densification process, this result is obtained at the expense of longer infiltration times in accordance with CVD results. Nevertheless, the benefits of this effect are also clear since as the overall densification rate diminishes, the densification rates in the different layers become similar.

The second set of experiments examined the effect of two different HCl concentration schedules. As described in section 5.2, the optimal use of the HCl effect occurs by the stepwise reduction of the HCl concentration from a sufficiently high initial level. This allows densification to proceed in a gradual fashion through the preform while preventing premature closure in the coldest sections (inlet). Several factors determine the optimal schedule, including the reactant concentrations, the initial HCl concentration, the length and number of steps, and the HCl concentration at each individual step. These parameters in turn depend on the temperature gradient and how it evolves through the preform as infiltration occurs. Obviously, knowledge of the later factors was not available; thus, the two schedules used could approach optimum conditions only coincidentally.

The first schedule begins with an initial mole % of HCl of 0.5. This HCl concentration is kept constant for 4hrs. Then, the HCl mole % is reduced to 0.1 and held constant for an additional 4 hrs. Finally, the HCl concentration is reduced to zero for the remainder of the infiltration. The second schedule starts with an initial concentration of 1

% for 3hrs, followed by 0.5 % HCl for 3 hrs, and then 0.1 % for also 3hrs. After this, infiltration continues without HCl.

The results of the two cases considered are summarized in table 5.3, and SEM cross sections are shown in figures 5.18-19. Although the overall residual porosity in case 2 is greater, the difference between layers is less compared to case 1. More uniformity is expected in case 2 because of the larger average HCl concentration throughout the infiltration. This argument explains the comparatively longer infiltration time in case 2 as well as the greater fractions of deposited matrix, initial porosity ultimately infiltrated, and their uniformity across different layers. Similarly, the densification rate is much lower, yet more uniform in case 2 as expected.

Comparison of the results from schedule 2 and the last infiltration in the first set of experiments (1% HCl throughout) indicates that more efficient densification is obtained in the latter case. This suggests that in schedule 2 the initial HCl concentration is too low. Thus, longer steps of greater HCl concentrations are necessary to raise the average concentration throughout the infiltration above 1%.

Table 5.3 Densification rates and efficiencies resulting from stepwise reduction of the HCl concentration.

<u>Schedule 1:</u> 0.5% HCl for 4 hours, 0.1% HCl for 4 hours, 0% HCl to completion.				
Overall Infiltration Time = 9.8 hours.				
Analysis Area	Fraction of Deposited Matrix (%)	Fraction of Residual Porosity (%)	Fraction of Infiltrated Initial Porosity (%)	Densification Rate (%/hr)
Top Layer	30.8	9.2	77.1	7.9
Middle Layer	33.1	10.7	75.6	7.7
Bottom Layer	47.5	6.6	87.7	9.0
Overall Sample	37.1	8.8	80.1	8.2
<u>Schedule 2:</u> 1% HCl for 3 hours, 0.5% HCl for 3 hours, 0.1% HCl for 3 hours, 0% HCl to completion.				
Overall Infiltration Time = 11.0 hours.				
Analysis Area	Fraction of Deposited Matrix (%)	Fraction of Residual Porosity (%)	Fraction of Infiltrated Initial Porosity (%)	Densification Rate (%/hr)
Top Layer	40.7	8.7	82.4	7.5
Middle Layer	35.6	8.6	80.6	7.3
Bottom Layer	48.1	11.9	80.2	7.3
Overall Sample	41.5	9.7	81.1	7.4

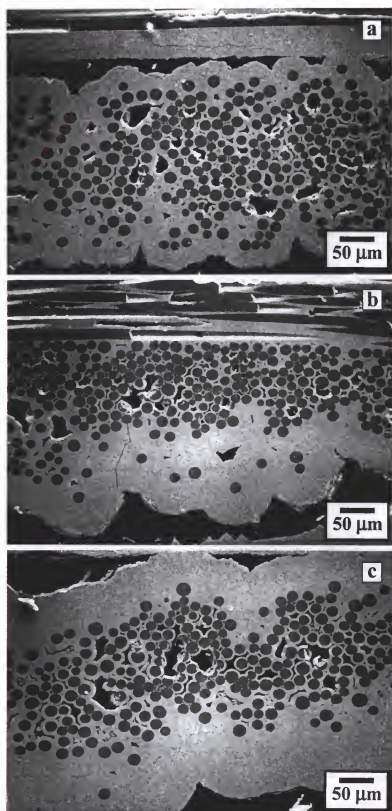


Figure 5.18 Forced-Flow Temperature Gradient CVI with Scheduled HCl Injection (Schedule 1).

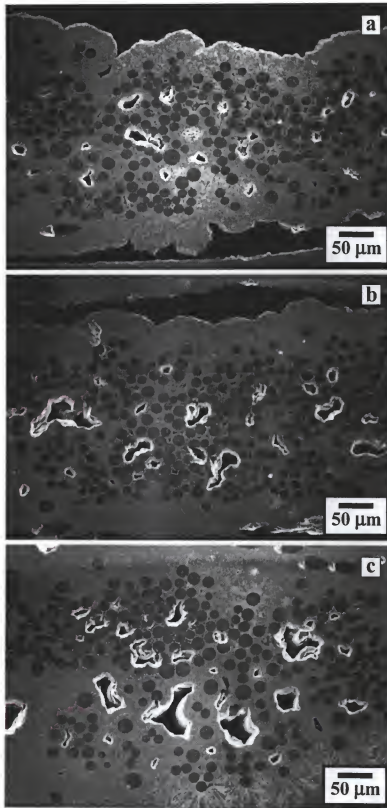


Figure 5.19 Forced-Flow Temperature Gradient CVI with Scheduled HCl Injection (Schedule 2).

CHAPTER 6

ATOMIC LAYER DEPOSITION OF TiC_x

6.1 Introduction

Toughening in ceramic-ceramic composites systems results when the fibers and matrix are weakly bonded at the interface [201]. This type of interaction promotes fiber pull-out which is one of the mechanisms responsible for crack absorption in toughened composites. Unfortunately, in some cases, a weak interface is not attainable without interface modification via application of an intermediate coating between the fibers and matrix. Such is the case of SiC -Nicalon composites whose interface is typically altered by depositing a submicron coating of graphitic carbon [204]. Since vapor synthesis techniques have been successfully used in many other coating applications, they are also an appealing choice for interface modification. An idea that is suggested by a method used in the deposition semiconductor materials, namely atomic layer epitaxy (ALE), was applied to composites [259-261].

The primary feature of ALE is that it theoretically allows deposition of a film one atomic layer at a time by taking advantage of the difference between the binding energies of physisorbed and chemisorbed species. Potentially, this digital mode of film growth can provide better control over film properties such as thickness, composition and microstructure. In addition, because only surface phenomena are involved in the growth process, ALE is insensitive to mass transfer effects, which is particularly useful in

the deposition of films within preform environments. Thus, in this chapter, the ALE of TiC_x and TiN will be investigated to assess the feasibility of this process to deposit thin films for interface modification. Naturally, coatings deposited in most ceramic applications are not epitaxial. Consequently, the name atomic layer deposition (ALD) has been used to describe this process for this application.

6.2 Theory and Operational Considerations

As mentioned, ALE is made possible by the difference between the two major mechanisms of adsorption, i.e., physical adsorption (physadsorption) and chemical adsorption (chemisorption) [262]. The first of these mechanisms is characterized by relatively weak Van der Waal bonding between the surface and adsorbate. It may result in multilayer coverage and is readily reversible. Chemisorption, on the other hand, involves the formation of a chemical bond (e.g., ionic or covalent bonds) which are significantly stronger than Van der Waal forces. A comparison of the stability of these two types of interaction is shown in figure 6.1, where the depth of the potential wells are representative of the strength of the respective bonds. Under certain conditions, chemisorption of only monolayer coverage is attainable, and desorption is not easily achieved. In relation to ALE, the difference between these two mechanisms become important as the surface temperature approaches a critical value [262]. Above this temperature, adsorbate bonds are "shaken off", leading to desorption of all but the strongly bonded chemisorbed layer. It is this feature that allows film growth in ALE to occur one atomic layer at a time.

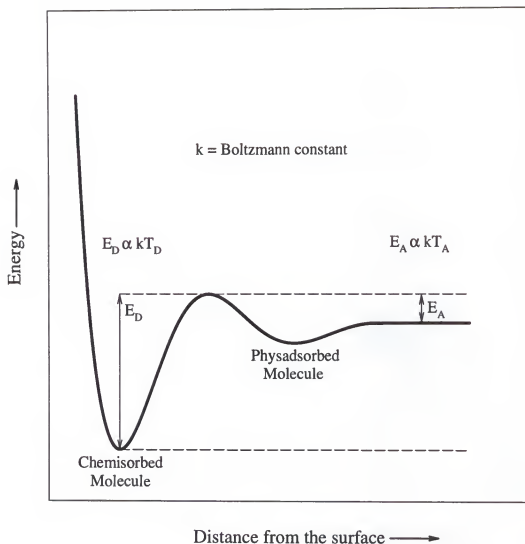


Figure 6.1 Potential energy diagram for physisorption and chemisorption.

There are two variations of ALE depending on whether elemental or molecular precursors are used [262]. The first variation, type I ALE, resembles molecular beam epitaxy (MBE) in that the film is deposited by a sequence of alternating pulses of elemental precursors. Each pulse is sustained long enough for the surface to reach equilibrium, and then followed by a period of vacuum or inert gas flush to reevaporate all physisorbed layers. Type II ALE, on the other hand, resembles CVD since instead of elements, molecular reactants with relatively high vapor pressures are used to deliver the

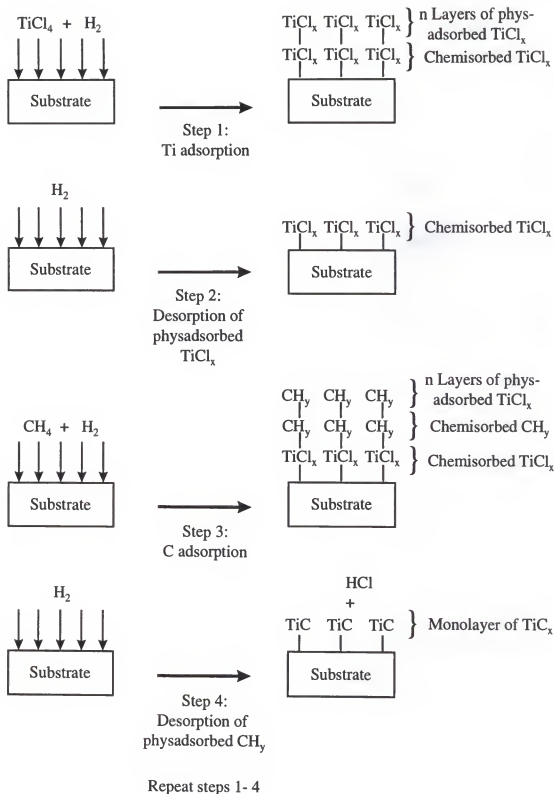


Figure 6.2 Cyclic steps in the ALE of TiC_x from TiCl_4 and CH_4 precursors.

film constituents to the surface. Figure 6.2 depicts this variation using the $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ chemistry to deposit TiC_x as example. Growth occurs by a sequence of surface reactions in which TiCl_4 is first adsorbed (step 1), followed by a flush period (step 2) to rid of the physisorbed material. CH_4 is then pulsed and allowed to react with the TiCl_x monolayer. After a second flush period (step 4), the result of the combined steps is a monolayer of TiC_x and the desorption of HCl . Further growth is achieved by repeating the above steps.

The use of type II ALE has allowed the extension of the technique to a wide variety of film chemistries not possible to the type I variant. For instance, films of Ta_2O_5 can not be deposited by type I ALE because Ta has such a low vapor pressure that desorption of excess Ta overlayers is not achieved at a reasonable temperature. By using volatile compound reactants such as TaCl_5 and H_2O , however, Ta_2O_5 can be obtained by type II ALE. Ironically, while molecular precursors have made type II ALE a versatile technique, they are also the cause for deviation from ideal ALE behavior. The steric hindrance resulting from large molecules adsorbing onto the surface means that monolayer coverage may require several process cycles. For example, ZnS growth from ZnCl_2 and H_2S proceeds at a rate of one layer per two cycles, while if $\text{Zn}(\text{CH}_3\text{COO})_2$ is used the rate drops further to a layer per three cycles [263]. On the other hand, multilayer growth per cycle has also been reported, as is the case for GaAs when metalorganic precursors are used [266].

From the above description, it is evident that the ALE process has several advantageous features, namely: a) the growth rate is not dependent on rates of reaction provided that the dose in each process step is large enough to give full monolayer

coverage [267]. Consequently, growth is uniform over large areas, and thickness monitoring is not necessary since film thickness is solely determined by the number of process cycles; b) the relatively high substrate temperatures results in the reevaporation of loosely bonded species from the surface. Together with the lack of vapor phase reactions, this leads to highly pure and stoichiometric films with few structural defects [265]; c) the growth process is entirely surface controlled, making ALE inherently insensitive to mass transfer effects [268].

Several factors influence optimal ALE operation. As discussed, the precursor materials must be volatile relative to the film at the substrate temperature. In addition, pulse intensities (partial pressures) and duration have to be large enough for equilibrium, and thus, monolayer coverage to be reached. On the other hand, reactant partial pressures should be considerably lower than their respective vapor pressures to avoid excessive condensation on the surface. An exceptional feature of ALE is that within the envelope set by the above requirements, reactant partial pressures can vary by several decades without any effect on the resulting film [263,265]. Optimization of growth temperature is, however, the most important consideration [262]. Since temperature determines which adsorption mechanism dominates the deposition process, it is important to use a high enough substrate temperature so that only chemisorbed layers remain after each flush step. Otherwise, the growth rate becomes a function of temperature and pulse intensities and duration. In most cases, however, the minimum temperature is set by the reactant condensation temperatures at the minimum partial pressures [265].

6.3 Previous Work

ALE was originally developed to improve the properties of electroluminescent devices. Consequently, initial research concentrated on II-VI and oxide materials [262,264]. Currently, materials fabricated by ALE include a wide variety of binary, ternary and quaternary compounds of the III-V and II-VI families (e.g., CdS, CdTe, ZnS, ZnSe, ZnTe, InAs, InP, GaP, GaN, GaAs, AlAs, ZnO, Ta₂O₅, TiO₂, SnO₂, Cd_{1-x}Mn_xTe, Zn_{1-x}Mn_xS, Cd_{1-x}Hg_xTe, Ga_{1-x}Al_xN, Ga_{1-x}In_xAs, Cd_{1-x}Hg_xTe_{1-y}Se_y) [269-273]. There is also increasing interest in using ALE to grow ceramic materials (e.g., TiN, NbN, MoN, TaN, Al₂O₃, SiC) and single crystal elemental films such as epitaxial Silicon [274-278]. Although no previous work on the ALE of TiC_x was found in the literature, the ALE of TiN has already been reported by Leskela et al [278,279]. ALE has also been researched as an alternative technique to CVD and MBE in several innovative applications, including: creation of abrupt interfaces, ultrathin quantum well structures, superalloys, selective area epitaxy, low temperature deposition and superlattices [267, 271, 273, 275, 280].

A specific instance of these applications is delta (atomic plane) doping [280]. In order to increase the transductance of field effect transistors, sheets of dopants (e.g., Se) are sandwiched within layers of intrinsic material (e.g., GaAs). This is known as delta or atomic plane doping, and its influence on the transductance is attributed to the electrons behaving as a two-dimensional gas due to their confinement at the impurity plane. Deposition of dopant layers of precise thickness is a task ideal for ALE. Delta doping of GaAs with Se has been reported, where a monolayers of Se are deposited on previously

ALE grown GaAs. The impurity planes are, subsequently, buried beneath additional ALE layers of GaAs.

Another application where ALE has been demonstrated to be superior to CVD and MBE is side wall epitaxy, i.e., the deposition of films on grooves, mesas and one-dimensional etch patterns [271]. Side wall epitaxy is used in several device concepts such as side wall FETs, MODFETs, and quantum wire structures. The use of CVD or MBE in these applications generally leads to film thickness variations on surfaces of different orientation. This is the result of changes in the sticking coefficient, angle impingement and mass transfer limitations at the inside surfaces. In principle, ALE is free of these problems, and is expected to yield uniform films inside these structures. This versatility of ALE has been demonstrated with the deposition of GaAs within 4 μm deep grooves etched in a GaAs substrate. The films were of uniform thickness at the bottom and side surfaces of the grooves, and defects were absent at the surface intersections.

6.4 Experimental

The ALE experiments were carried out in the apparatus described in chapter 3. A gas chromatography switching valve was used to pulse the reactants. Pulse duration, pulse sequence, and number of cycles were automatically controlled by computer. To prevent pressure surges during pulsing, flows other than those involved in the immediate pulse were diverted by the switching valve to an alternate reactor vessel. This maintained a dynamic balance on all reactant and flush flows. The precursor chemistry used for TiC_x deposition was the same to that described in chapter 3. A typical TiC_x ALD cycle involved pulsing 1 to 2 mole % CH_4 in H_2 for 1 to 2 sec., followed by a 10-sec. flush

with H_2 . 1 to 2 mole % $TiCl_4$ in H_2 was then pulsed for 1 to 2 sec., once again followed by a 10-sec. flush with H_2 . Thus, the total cycle time was 22 to 24 sec. The total number of cycles were from 50 to 100.

TiN ALD cycles were also composed of steps of similar duration; however, electronic grade NH_3 was employed instead of CH_4 in the first step. The total number of cycles ranged from 200 to 400. In addition, the concentrations of the reactant pulses were lower, varying from 0.05 to 1 mole % for $TiCl_4$ and 0.5 to 1.5 mole % for NH_3 . The reactor temperature and pressure were varied from 400 to 1000 °C and 50 to 760 Torr respectively. TiC_x depositions were performed on electronic grade polycrystalline Al_2O_3 substrates, while TiN films were deposited on Nb foils.

6.5 Results and Discussion

The expected theoretical thickness per cycle of TiC_x and TiN films is on average 4.2 to 4.3 Å. From the total cycle time given above, the average theoretical growth rate of these films by ALD was approximately 0.2 Å/s. In comparison, the measured growth rate of TiC_x by CVD was on average 14 Å/s. This order of magnitude difference is typical as the growth rate in ALD is limited by the overall cycle time. A typical morphology of TiC_x ALD films is shown in Figure 6.3. The films are fairly uniform with a grain size smaller than that of the substrate. XRD was used to identify the film chemistry; however, only peaks representative of the substrate were detected due to the limited thickness of the deposits. As a result, the films were analyzed by XPS since this technique is primarily surface sensitive. Figure 6.4a shows a characteristic XPS spectrum of an as deposited sample. Peaks corresponding to Ti, C and O were detected. To determine whether the

observed oxide and carbon were just a surface occurrence, the films were sputtered with Ar for 5 min. The spectrum obtained after sputtering is shown in figure 6.4b. Once again, only Ti, C and O were detected, indicating an oxycarbide composition throughout. Interestingly, the carbon signal is also seen to decrease, while the oxygen peaks intensify. This increase may be attributed to contributions from the Al_2O_3 substrate. Since XPS analysis is ex-situ, it is not clear whether the oxygen in the films originates from contamination in the reactor chamber or from adsorption of oxygen from the atmosphere after removal from the reactor. Since the oxygen content of the films is significant, it is unreasonable to expect that the source of contamination is ambient oxygen as the rate of adsorption is extremely low at ambient temperature. Therefore, it can only be concluded that oxygen inclusion occurs during processing of the films, and that the oxygen originates, perhaps, from an unidentified equipment leak.

The morphology of TiN deposits on Nb foils is shown in figure 6.5. In this case, the depositions begin with the formation of a continuous film followed by cluster development. This may be explained by the use of a relatively high operating temperature which then leads to uncontrolled nucleation phenomena characteristic of CVD. XPS spectra of as deposited TiN films is shown in figure 6.6a. Peaks corresponding to Ti, C and O were detected, yet N was not found in the as deposited sample. After 30 min. of Ar sputtering, the surface carbon contamination disappears (see figure 6.6b). In addition, there is a decrease in the O_{1s} oxygen peak, and the appearance of a nitrogen signal. The formation of an oxynitride film is, again, the result of the presence of oxygen contamination in the reactor chamber during processing. As with the TiC_x films, the oxygen is believed to reach the reactor through an equipment leak.

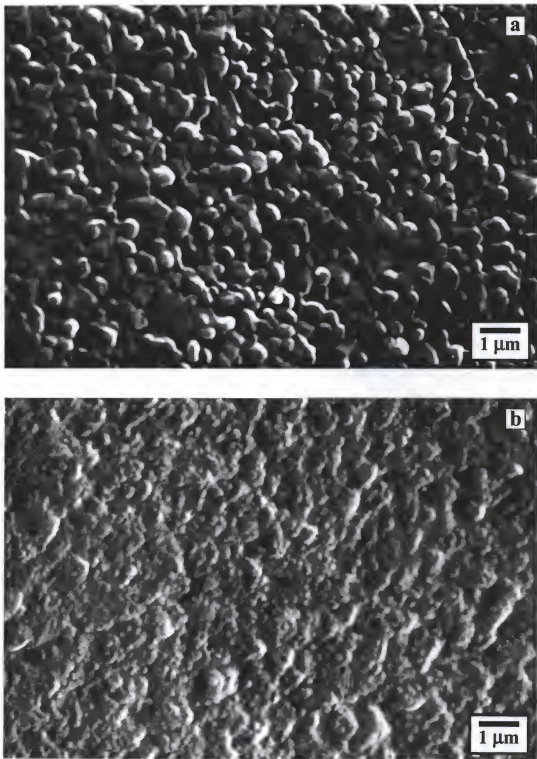


Figure 6.3 Surface Morphology of a) Al_2O_3 substrate prior to ALD and b) TiC_x Coating deposited by ALD.

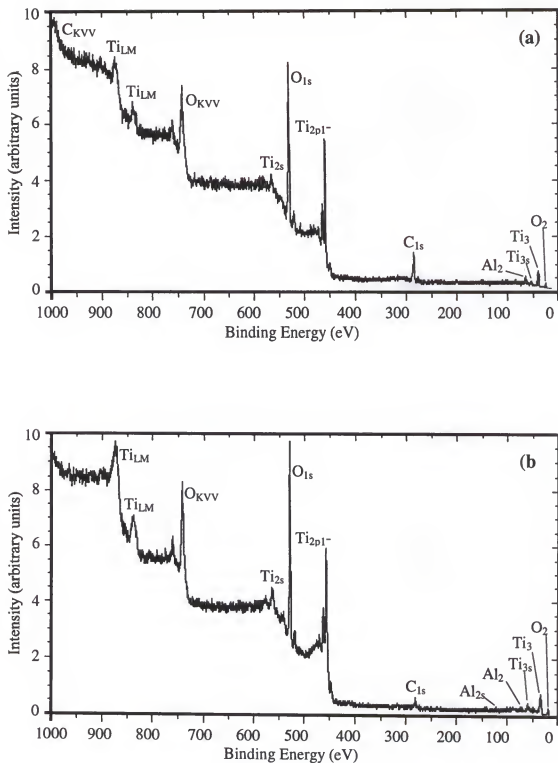


Figure 6.4 XPS survey of TiC_x film deposited on polycrystalline Al_2O_3 by ALD. a) film surface after deposition; b) film surface after 5 minutes of Ar^+ sputtering.

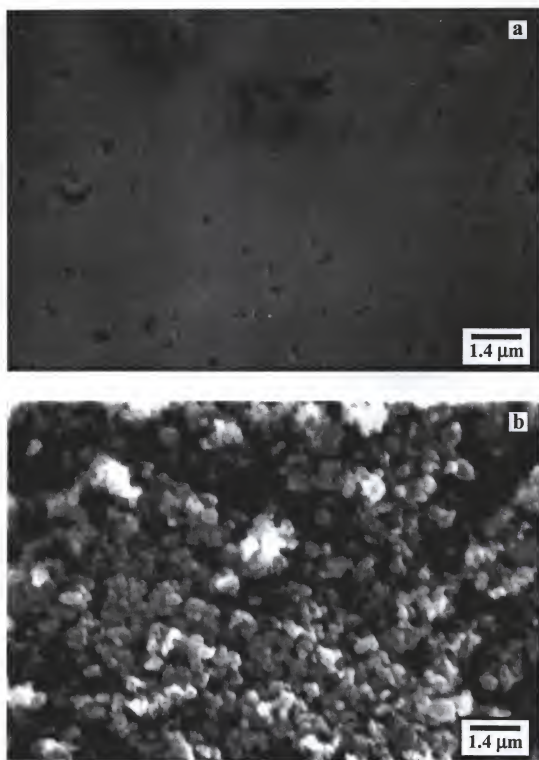


Figure 6.5 Surface Morphology of a) Nb substrate prior to ALD and b) TiN Coating deposited by ALD.

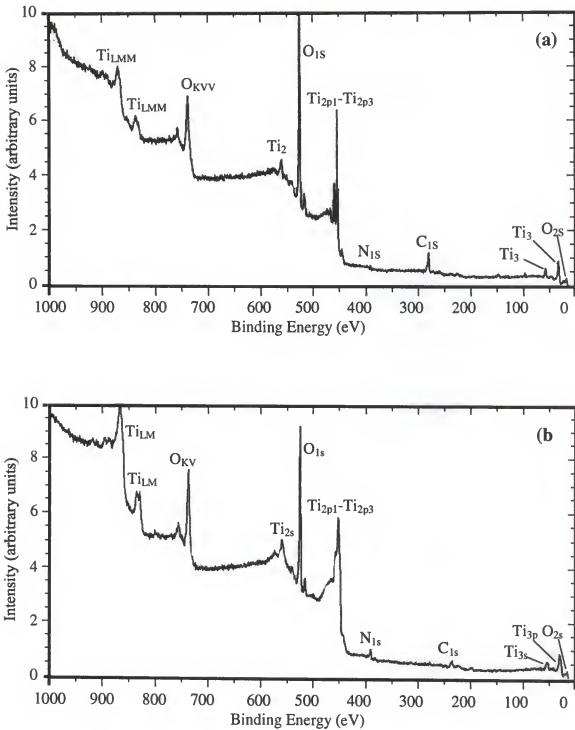


Figure 6.6 XPS survey of TiN film deposited on Nb by ALD.

a) film surface after deposition; b) film surface after 30 minutes of Ar⁺ sputtering.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1 Conclusions

The CVD and ALD of TiC_x coatings on flat substrates and the CVI of continuous ceramic fiber preforms with TiC_x were investigated. The purpose of this study was to explore fundamental and experimental aspects of these processes to improve upon existing ceramic-matrix composite vapor synthesis techniques. The first step in both the CVD and CVI investigations was to model the respective processes in order to corroborate a priori assumptions and guide subsequent experimental work.

Accordingly, equilibrium modeling of TiC_x CVD from TiCl_4 - CH_4 - H_2 precursors revealed a wide range of precursor compositions over which TiC_x can be deposited as a single phase compound. The variation in TiC_x stoichiometry with reactant composition in this homogeneity region was also predicted by the model; however, significant discrepancies were observed between the model predictions and experimentally measured film compositions. These differences can be attributed to kinetic limitations which can be expected in a dynamic process such as CVD. The model also revealed the existence of two-phase regions where limiting stoichiometries of TiC_x are co-deposited with either graphite or β -Ti. The graphite co-deposition region occurs generally at high CH_4 concentrations while the β -Ti region occurs at low concentrations of both CH_4 and TiCl_4 . In addition, the width of the single phase TiC_x region was found to decrease with

increasing temperature which is reasonable since increasing concentrations of vacancies are expected at higher temperature.

The injection of HCl as a reactant was found to decrease the extent of TiC_x formation as predicted by the Le'Chatelier principle. An examination of the equilibrium vapor phase indicates that the reduction in the solid TiC_x equilibrium yield when HCl is injected is caused by an increase in the volatility of titanium subchloride species. It was also determined that the etching effectiveness of HCl decreases with increasing temperature. Thus, while it is possible to completely prevent the formation of TiC_x by using sufficiently high HCl concentrations, this effect is modulated by temperature. The locus of all temperatures and HCl concentrations determining this condition forms an etch-deposition boundary separating operating zones where TiC_x is produced or not. In general, deposition of TiC_x is favored by high temperature and low concentration of HCl.

The deposition rate of TiC_x from $\text{TiCl}_4\text{-CH}_4\text{-H}_2$ reactants on flat polycrystalline and single crystal (0001) and (1 $\bar{1}$ 02) Al_2O_3 substrates was kinetically limited for total flow rates above 1000 sccm and temperatures below 1573 K. An Arrhenius dependence of the deposition rate with temperature was found not only for the above substrates, but also for depositions on Nicalon fibers, and graphite and Ta substrates. Significant differences in the measured activation energies for deposition on these substrates points to a surface controlled process under the studied conditions. The same conclusion can be drawn from the notable differences in microstructures and preferred orientations of TiC_x grains observed which vary as a function of both substrate and deposition temperature.

The dependence of the deposition rate on the reactant concentrations appears to follow a two-site adsorption mechanism where the rate initially increases linearly, reaches

a maximum and then decreases with respect to either of the reactant concentrations. This behavior holds for the variation of the rate with the TiCl_4 concentration; however, only the linear aspect of this dependence is observed in the case of CH_4 for the conditions used. The addition of HCl to the reactant mixture causes a decrease in the deposition rate at relatively low concentrations of HCl . As the HCl concentration increases beyond a certain limit the rate becomes constant. This behavior is attributed to etching of graphite components in the reactor and the consequent increase in concentration of carbon containing vapor species which tends to accelerate the deposition rate.

A single cylindrical pore geometry was used to model the effect of process parameters on the CVI of TiC_x . Although the model was far from approximating a real CVI process, it predicted fairly well general trends in the infiltration rate and efficiency as infiltration parameters were changed. The model demonstrated that higher infiltration efficiency results when a combination of relatively lower infiltration temperature and pressure are used, a result corroborated by experiment. The use of a temperature gradient produced similar results on the amount of residual porosity. Most importantly, the model also predicted that the application of a temperature gradient in tandem with injection of HCl as a reactant leads to even higher infiltration efficiencies than with the use of a temperature gradient alone.

Infiltration of Nicalon preforms with TiC_x using a type II CVI scheme resulted in extremely low levels of densification even after infiltration for 36 hrs. The use of a forced-flow temperature-gradient CVI scheme led to greater densification levels in shorter infiltration times. Despite the transport limitations imposed by the preform, densification is still affected by the reaction kinetics, as evidenced by the changes in

densification rate with the reactant ratio. The rate of densification increases with increasing gas velocities as more material is available for reaction. However, above a total flow rate of 750 sccm, the overall process becomes kinetically controlled. Thus, the densification rate decreases as the reactant residence time drops with increasing gas velocities.

The use of increasing concentrations of HCl in the reactant mixture reduces the fraction of residual porosity in the overall final composite as well as in the three weave layers comprising the preform. In addition, the use of HCl improves the density uniformity across the composite sections. These effects, however, occur at the expense of lower densification rates, as indicated by longer infiltration times. From this evidence and previously discussed model results, it can be concluded that composite density uniformity can be improved by devising a new CVI scheme where a temperature gradient is used with decreasing concentrations of injected HCl. This scheme allows enhanced control over the infiltration than techniques that use a temperature gradient alone. The use of HCl schedules during infiltration using a temperature gradient corroborate this deduction. Further optimization of this process is, however, necessary, particularly the use of higher average concentrations of inlet HCl, in order to favorably compare its promise versus optimized variations of existing CVI processes.

XPS characterization of TiC_x films deposited on polycrystalline Al_2O_3 by ALD revealed a titanium oxy-carbide composition. The contamination is attributed to adsorption of oxygen into the films during processing from an unknown source, perhaps an equipment leak. The fact that TiC_x has a tendency to exhibit large fractions of vacancies, makes it difficult to obtain pure films particularly in the thickness range

produced by ALD. Thus, the presence of oxygen during deposition at temperatures above ambient inevitably leads to the formation of an oxide. Similarly, TiN films deposited on Nb exhibited oxygen contamination. Once again, the oxide formation is explained by the same arguments stated above.

7.2 Recommendations for Future Work

a) **Use of differential in-situ gravimetry for precise determination of the kinetics of TiC_x deposition:** Perhaps the single most important factor limiting the accuracy of model results and the optimization of CVI processes is the lack of reliable kinetic data. The scope of this work only included a partial attempt at determining the kinetics of TiC_x deposition. In addition, the method of measuring weights before and after deposition only reveals an average deposition rate which masks phenomena characteristic of the early stages of growth, and thus nucleation behavior. The technique of in-situ differential gravimetry using micro-balances has been used successfully by other authors to obtain a wealth of kinetics information with minimal time expenditure in systems such as: $\text{TiCl}_4\text{-C}_3\text{H}_8\text{-H}_2$ and $\text{SiCl}_4\text{-CH}_4\text{-H}_2$ [165,196]. It is recommended that this technique be adopted to gain a precise handle on the kinetics of TiC_x deposition.

b) **Improvement of the thermodynamic equilibrium algorithm:** Further refinements are necessary for the thermodynamic equilibrium algorithm in appendix 1. Difficulties still remain when dealing with complex systems which require the simultaneous consideration of several pure single-species phases along with a non-ideal condensed phase solution. Of particular concern is the inability of the program to deal with trace species together with the principal equilibrium system. Routines such as the

original VCS algorithm use a method of separating trace species from the principal equilibrium system, and considering the changes in their mole numbers during intermediate iterations independently [224]. When the mole numbers of any of these species increases above a threshold value it is automatically included in the main calculation. The adoption of this technique may accelerate the convergence speed of the program and increase the accuracy of the equilibrium results. The indirect scheme described in chapter 2 was successfully used to determine the equilibrium of the TiC_x binary solid solution. It would be useful to extend this technique to consider condensed solution systems with degrees of freedom greater than one.

c) **Alternative models of CVI:** The single cylindrical pore model in chapter 4 was a highly simplified attempt at assessing the behavior of the densification rate and efficiency in response to the CVI parameters, particularly the injection of HCl. Perhaps, the first step in refining this approach would be to consider a numerical solution to the equations of change which does not ignore phenomena such as dispersion in the axial direction. The use of a comprehensive model can then be used in combination with experimental results to alternatively extract data on the kinetics of deposition. The creation of ceramic capillaries to examine the infiltration of single cylindrical pores has been discussed by Naslain et al. [247]. Any intermediate model attempt which does not consider a detailed dynamic description of the preform porosity evolution during infiltration is not recommended. Such attempts have consistently fallen short of explaining experimental results.

d) **Modification of the CVI reactor design:** The reactor used to carry out the CVI experiments is a derivative of a conventional CVD reactor which is not entirely

suitable for CVI operation. It is recommended that a hot wall (furnace heated), all-metal-encased design be used. During several experiments the limits of the r.f. generator power output were reached precluding infiltration at the desired temperature set-point. The use of metal components would not only enhance safety, but also allow operation at pressures higher than atmospheric, thus permitting a greater degree of densification. Furthermore, metallic components in the injector-holder set-up would allow the use of a water cooled jacket, a feature used by the ORNL process to enhance the temperature gradient. More importantly, the sample holder should be designed to handle preform samples of at least three inches in diameter. This is considered the limiting size of the bar samples used for meaningful mechanical testing of the composite.

e) **Optimization of the HCl injection CVI scheme:** Further work is necessary to optimize the HCl injection scheme in order to compare its capability versus other processes such as the ORNL scheme. From the results of chapter 5, it is clear that concentration schedules with higher average concentrations of HCl are necessary. Optimum schedule parameters such as the number, duration and intensity of the concentration steps must be determined. This is a difficult empirical task, and the usefulness of a comprehensive CVI model becomes evident. Since the success of the CVI scheme is dependent on the evolution of the temperature gradient, it is incumbent to characterize the changes in the preform thermal properties as infiltration occurs.

f) **Use of C_3H_8 as alternative hydrocarbon source:** The specific motivation to select this precursor is that C_2H_2 pyrolyzes in an exothermic fashion. This reaction behavior enhances the effect of the temperature gradient by providing an additional thermal source at the reaction front.

g) **Study of the ALD of BN as interface modification coating:** BN has been studied as an oxidation resistant alternative to graphite for interface modification purposes [214]. BN is not susceptible to oxygen contamination as are compounds with large fractions of vacancies; thus films reasonable purity can be obtained. The ALD of this chemistry can be first demonstrated on flat substrates, and then extended to preform environments where the technique then becomes a derivative of isothermal pulsed CVI.

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APPENDIX 1 **FORTRAN SOURCE CODE OF MODIFIED EQUILIBRIUM ALGORITHM**

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C OPTIMIZED STOICHIOMETRY ALGORITHM WITH INDIRECT BINARY
C NON-IDEAL SCHEME.
C
C
C   DIMENSION A(55,13),A0(55),A1(55),A2(55),A3(55),COEFF(6),D(13,13),
&   DINV(13,13),DD(13,13),DH0(55),DS0(55),GNU(55,13),
&   ICP(55),IDXBAS(13),INDEX(55),INERT(3),STDCP(55),
&   TOTMC(55),WKA(55),IREAC(13)
C   INTEGER BSPCE(55,3),ISPCE(55,3),PHASE(55,3),SPECIE(55,3),
&   STRING(6,4),TITLE(20),V,S,C,E,VP1,VPS,VSP1,VSC,VSCE,
&   BQUES(55),QUES(55),QUEST1/'? '/,QUEST2/'?? '/,
&   ELMNT(13)/13*' '/,VAPOR(3)/' V','APO','R '/,
&   SOLN(3)/'SOL','UT','ON '/,COND(3)/'CON','DEN','SED'/,
&   RPSPS/'/'/,RPAS/'<='/'/,RPBL/'/'/,SSPS/'+'/,
&   BLNKS/'/'/,LP/'/'/,BASIS(55,3)
C   REAL*8 DD,DINV,WKA,N(55),BESTN(55),NTEMP(55),DPRME(13,13),
&   Q(55),KEQ(55),FRAC(55),FRACIN(55),DZETA(55),LAMBDA,
&   RLXMIN,B(13),BCALC(13),ARG,CHMPT(55),STP,CHM,DG(55),
&   RELERR,F1,F2,FREE,GFE,ACOE(55),FRACO(4),FRACON,BMOLE,
&   FRACRA,FRACBASE,FRACERR,FRACCU,FRACLIM,DMFF,DMFI,
&   DMFLO,DMFHI,FS1,ERRDMF,GAM
C
C A(I,J) : ELEMENTAL ABUNDANCE MATRIX
C B(J) : TOTAL NUMBER OF GRAM-MOLES OF ELEMENT J
C DH0(I) : ENTHALPY OF FORMATION OF SPECIES I
C DS0(I) : ENTROPY OF FORMATION OF SPECIES I
C STDCP(I) : STANDARD CHEMICAL POTENTIAL OF SPECIES I
C
C ***** HEAT CAPACITY CORRELATIONS *****
C ICP(I)=0 :  $CP(I) = A0(I) + A1(I)*T + A2(I)/T**2 + A3(I)*ALOG(T)$ 
C ICP(I)=1 :  $CP(I) = A0(I) + A1(I)*T + A2(I)*T**2 + A3(I)*T**3$ 
C ICP(I)=2 :  $CP(I) = A0(I) + A1(I)*T + A2(I)*T**2 + A3(I)/T**2$ 
C
C   OPEN(UNIT=5,FILE='CHOSPEC.DAT',STATUS='OLD')
C   OPEN(UNIT=2,FILE='WRAPUP.DAT',STATUS='NEW')

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OPEN(UNIT=6,FILE='MCMOUT.DAT',STATUS='NEW')
IRD=5
IWRT=6
IFILE=2
IDIM1=55
IDIM2=13
FRCZIN=0.0
DH0Z=0.0
DS0Z=0.0
A0Z=0.0
A1Z=0.0
A2Z=0.0
A3Z=0.0
TOTMV=0.0
C
C READ TITLE
C
  READ(IRD,5) (TITLE(K),K=1,20)
  5 FORMAT(20A4)
C
C NUMBER OF ELEMENTS, VAPOR SPECIES, SOLUTION SPECIES,
C CONDENSED PURE PHASES, SYSTEM TEMPERATURE (K) AND PRESSURE
C (PA)
C
  READ(IRD,10) E,V,S,C,T,P,T0,P0,IX
  10 FORMAT(4I5,4F10.0,I5)
  VP1=V+1
  VPS=V+S
  VPSP1=V+S+1
  VSC=V+S+C
  VSCE=V+S+C+E
C
C READ ELEMENTS
C
  READ(IRD,15) (ELMNT(J),J=1,E)
  15 FORMAT(13(1X,A2))
C
C VAPOR SPECIES INFORMATION
C
  IF(V.EQ.0) GO TO 118
  DO 110 I=1,V
  READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
  READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
  READ(IRD,22) (A(I,J),J=1,13)

```

```

20 FORMAT(3A4,2E12.5)
21 FORMAT(4E12.5,I2)
22 FORMAT(13(F5.0,1X))
    DO 110 J=1,3
        PHASE(I,J)=VAPOR(J)
110 CONTINUE
C
C INERT SPECIE
C
    READ(IRD,20) (INERT(K),K=1,3),DH0Z,DS0Z
    READ(IRD,21) A0Z,A1Z,A2Z,A3Z,ICPZ
    READ(IRD,22) DUMMY
118 CONTINUE
C
C SOLUTION SPECIES INFORMATION
C
    IF(S.EQ.0) GO TO 125
    DO 120 I=VP1,VPS
        READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
        READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
        READ(IRD,22) (A(I,J),J=1,13)
        DO 120 J=1,3
            PHASE(I,J)=SOLN(J)
120 CONTINUE
125 CONTINUE
C
C CONDENSED PHASE DATA
C
    IF(C.EQ.0) GO TO 135
    DO 130 I=VPSP1,VSC
        READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
        READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
        READ(IRD,22) (A(I,J),J=1,13)
        FRAC(I)=1.0
        FRACIN(I)=1.0
        DO 130 J=1,3
            PHASE(I,J)=COND(J)
130 CONTINUE
135 CONTINUE
C
C READ ADDITIONAL REFERENCE SPECIES TO COMPUTE ST. ST. CHEM.
C POT.
C
    IF(IX.EQ.0) GO TO 131

```

```

DO 132 I=VSC+1,VSC+IX
READ(IRD,20) (SPECIE(I,K),K=1,3),DH0(I),DS0(I)
READ(IRD,21) A0(I),A1(I),A2(I),A3(I),ICP(I)
READ(IRD,22) (A(I,J),J=1,13)
132 CONTINUE
131 CONTINUE
C
C MAXIMUM NUMBER OF ITERATIONS, CONVERGENCE CRITERION AND C
C OPTIONS
C
READ(IRD,136) IDEBUG, IOPT, ISS, IWRAP, MAXIT, NMAX, CNVG, TINC, NCL, PINC,
&      RLXMIN
136 FORMAT(6I5,E10.1,F10.1,I5,F5.1,F10.1)
C-----
READ(IRD,176) ICOML,ISP1,ISP2,ISP3,ISP4,ISPL1,ISPL2,IFCOMP,CLOOP1,
&      SCLP1,CLOOP2,SCLP2
176 FORMAT(8I3,4E12.5)

READ(IRD,177) NTBOU,IB,SFF,FRACCU,FRACLIM,IREDIS,IRE1,IRE2,SOLMOL,
&      ICU
177 FORMAT(2I3,F5.1,2E12.5,3I3,E12.5,I3)
C-----
ISPLL=ISP1
IF(SFF.LT.0.0) THEN
  IF(IWRAP.EQ.7) WRITE(IFILE,2100)
2100  FORMAT(1X,'INLET COMPOSITIONS WHERE TIC + C BOUNDARY
&OCCURS')
  WRITE(IFILE,*) ' '
  ELSEIF(SFF.GT.0.0) THEN
  IF(IWRAP.EQ.7) WRITE(IFILE,2130)
2130  FORMAT(1X,'INLET COMPOSITIONS WHERE TI + TIC BOUNDARY
&OCCURS')
  WRITE(IFILE,*) ' '
  ELSE
  ENDIF
C-----
IF(IWRAP.EQ.3) IFILE=IWRT
C
C CREATE A TABLE FILE IF LOOP OPTIONS ARE CHOSEN
C
IF(IOPT.NE.0) OPEN(UNIT=7,FILE='TABLE.DAT',STATUS='NEW')
ITAB=7
C

```

```

C SET THE LOOP LIMITS FOR THE TEMPERATURE, PRESSURE AND
COMPOSITION
C LOOPS. THE COMPOSITION LOOP STARTS HERE
C
  NCMP=1
  NTP=1
  IF(IOPT.EQ.1.OR.IOPT.EQ.2) NTP=NMAX
  IF(IOPT.EQ.3) NCMP=NMAX
  IF(IOPT.EQ.4.OR.IOPT.EQ.5) NTP=NMAX
  IF(IOPT.EQ.4.OR.IOPT.EQ.5) NCMP=NCL
  DO 2000 ICMP=1,NCMP
C-----
    WRITE(*,*) ' '
    IF(NCMP.GT.1) WRITE(*,*) 'COMPOSITION LOOP #',ICMP
    WRITE(*,*) ' '
C-----
C
C TOTAL NUMBER OF MOLES OF VAPOR AND MOLE FRACTIONS
C
  IF(V.EQ.0) GO TO 138
  READ(IRD,137) TOTMV
  READ(IRD,137) (FRACIN(I),I=1,V),FRCZIN
137 FORMAT(6E12.5)
C
C TOTAL NUMBER OF MOLES OF SOLUTION SPECIES, MOLE FRACTIONS
C AND EXCESS FREE ENERGY CORRELATION PARAMETERS
C
138 CONTINUE
  IF(S.EQ.0) GO TO 140
  READ(IRD,137) TOTMS
  READ(IRD,137) (FRACIN(I),I=VP1,VPS)
  READ(IRD,139) IXSCOR,AXS,BXS
139 FORMAT(I5,2E12.5)
140 CONTINUE
C
C TOTAL NUMBER OF MOLES IN PURE CONDENSED PHASES
C
  IF(C.EQ.0) GO TO 142
  READ(IRD,137) (TOTMC(I),I=VPSP1,VSC)
142 CONTINUE
C-----
C REDISTRIBUTE INITIAL TI AND C FROM CH4 AND TICL4 TO THE SOLID.
C
  IF(IREDIS.EQ.0) GO TO 143

```

```

TOTMS=SOLMOL
DTIS=TOTMS*FRACIN(IRE1)
DCS=TOTMS*FRACIN(IRE2)
DCH4=TOTMV*FRACIN(ISP1)-DCS
DTICL4=TOTMV*FRACIN(ISP2)-DTIS
DHCL=4.0*DTIS
SIGN=1.0
IF(DCS.EQ.DTIS) SIGN=0.0
DH2=2.0*SIGN*(DCS-DTIS)+TOTMV*FRACIN(ISP4)
TOTMV=DCH4+DTICL4+DHCL+DH2
FRACIN(ISP1)=DCH4/TOTMV
FRACIN(ISP2)=DTICL4/TOTMV
FRACIN(ISP3)=DHCL/TOTMV
FRACIN(ISP4)=DH2/TOTMV
IF(FRACIN(IRE1).LE.0.0) FRACIN(IRE1)=1.0E-40
IF(FRACIN(IRE2).LE.0.0) FRACIN(IRE2)=1.0E-40
IF(FRACIN(ISP1).LE.0.0) FRACIN(ISP1)=1.0E-40
IF(FRACIN(ISP2).LE.0.0) FRACIN(ISP2)=1.0E-40
IF(FRACIN(ISP3).LE.0.0) FRACIN(ISP3)=1.0E-40
IF(FRACIN(ISP4).LE.0.0) FRACIN(ISP4)=1.0E-40
143 CONTINUE
C-----
C BEGIN TEMP LOOP FOR BOUNDARY COMPUTATION
C
  FRACO(1)=FRACIN(ISP1)
  FRACO(2)=FRACIN(ISP2)
  FRACO(3)=FRACIN(ISP3)
  FRACO(4)=FRACIN(ISP4)
  JTBOU=0
7000 JTBOU=JTBOU+1
  IF(JTBOU.GT.1) T=T+TINC
  WRITE(IFILE,2110) T
2110 FORMAT(/,1X,'TEMP(K)=',F7.1)
  WRITE(IFILE,*) ' '
  IF(IWRAP.EQ.7) WRITE(IFILE,2120)
2120 FORMAT(4X,'XCH4',8X,'XTICL4')
  IF(IWRAP.EQ.8) WRITE(IFILE,2121)
2121 FORMAT(4X,'XTICL4',8X,'XCH4',8X,'C/TI')
C-----
C BEGIN LINE COMPOSITION LOOP
C
  RSC1=1.0/SCLP1
  RSC2=1.0/SCLP2
  NSCLP1=INT(RSC1)

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```

NSCLP2=INT(RSC2)
IF(ICOML.EQ.0.) ISPL1=1
IF(ICOML.EQ.0.) ISPL2=1
IF(ICOML.EQ.0.OR.IFCOMP.NE.3) NSCLP1=1
IF(ICOML.EQ.0.OR.IFCOMP.NE.3) NSCLP2=1
DO 5100 ICOMP1=1,ISPL1
DO 5200 ISCOMP1=1,NSCLP1
IF(IFCOMP.EQ.3.AND.ICOMP1.EQ.ISPL1.AND.ISCOMP1.GT.1) GO TO 5200
DO 5300 ICOMP2=1,ISPL2
DO 5400 ISCOMP2=1,NSCLP2
IF(IFCOMP.EQ.3.AND.ICOMP2.EQ.ISPL2.AND.ISCOMP2.GT.1) GO TO 5400
C-----
C
C SAVE THE ORIGINAL SPECIE ORDER SO THE PROBLEM
C CAN BE PLACED IN THIS ORDER AFTER THE ITERATIVE PROCEDURE
C
DO 165 I=1,VSC
DO 165 K=1,3
ISPCE(I,K)=SPECIE(I,K)
165 CONTINUE
C-----
C CHANGE INLET GAS MOLE FRACTIONS ACCORDING TO LINE
COMPOSITION LOOP
C
IF(ICOML.EQ.0) GO TO 188
IF(IFCOMP.EQ.1)THEN
FRACIN(ISP1)=FRACO(1)+(ICOMP1-1)*CLOOP1
FRACIN(ISP2)=FRACO(2)+(ICOMP2-1)*CLOOP2
ELSEIF(IFCOMP.EQ.2)THEN
ICPO1=(ICOMP1-1)
ICPO2=(ICOMP2-1)
FRACIN(ISP1)=FRACO(1)*CLOOP1**ICPO1
FRACIN(ISP2)=FRACO(2)*CLOOP2**ICPO2
ELSE
ICPO1=(ICOMP1-1)
ICPO2=(ICOMP2-1)
SCOMP1=(1.0-(ISCOMP1-1)*SCLP1)
SCOMP2=(1.0-(ISCOMP2-1)*SCLP2)
FRACIN(ISP1)=FRACO(1)*SCOMP1*CLOOP1**ICPO1
FRACIN(ISP2)=FRACO(2)*SCOMP2*CLOOP2**ICPO2
ENDIF
FRACIN(ISP4)=1.0D+00-FRACIN(ISP1)-FRACIN(ISP2)-FRACIN(ISP3)
188 CONTINUE
C-----

```

C BEGIN ITERATIVE PROCEDURE TO DETERMINE CVD DIAGRAM
 BOUNDARIES AS A
 C FUNCTION OF THE INLET GAS COMPOSITION
 C

IBL=0

I1=0

I2=0

2200 WRITE(*,2207) T,FRACIN(ISP1),FRACIN(ISP2)

2207 FORMAT(/,1X,'TEMP= ',F7.1,3X,'XCH4= ',E10.3,3X,'XTICL4= ',E10.3)

WRITE(*,*) ' '

IF(ICOML.NE.0) FRACIN(ISP4)=1.0D+00-FRACIN(ISP1)-FRACIN(ISP2)

& -FRACIN(ISP3)

IBL=IBL+1

C-----

IDATA=0

IF(ICMP.GT.1.OR.IWRAP.EQ.3.OR.IWRAP.GE.7) GO TO 187

C

C WRITE-OUT SOME OF THE INPUT DATA

C

IPAGE=1

WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE

WRITE(IWRT,410) T,P

IF(IWRAP.GT.1) GO TO 187

WRITE(IWRT,170)

170 FORMAT('0',1X,T55,'HEAT CAPACITY CORRELATION COEFFICIENTS',

&,1X,T16,'ENTHALPY OF',T33,'ENTROPY OF',T58,'ICP=0: CP = A0',

&' + A1*T + A2/T**2 + A3*LN(T)',1X,T17,'FORMATION',T33,'FORMAT',

&'ION',T58,'ICP=1: CP = A0 + A1*T + A2*T**2 + A3*T**3',1X,T58,

&'ICP=2: CP = A0 + A1*T + A2*T**2 + A3/T**2',1X,T4,

&'SPECIE',T20,'DH0',T37,'DS0',T54,'A0',T73,'A1',T93,'A2',T113,

&'A3',T122,'ICP',1X,T4,'SYMBOL',T15,'(KCAL/G-MOLE)',T30,

&'(KCAL/G-MOLE-K)',T47,'(KCAL/G-MOLE-K)',T65,'(KCAL/G-MOLE-K**2)',

&T86,'(.....)',T106,'(.....)',T122,'(-)',

&/',+',12(' '),T15,13(' '),T30,15(' '),T47,15(' '),

&T65,18(' '),T86,15(' '),T106,15(' '),T122,3(' '))

DO 180 I=1,VSC

WRITE(IWRT,175) (SPECIE(I,K),K=1,3),DH0(I),DS0(I),A0(I),A1(I),

& A2(I),A3(I),ICP(I)

IF(IEQ.V) WRITE(IWRT,175) (INERT(K),K=1,3),DH0Z,DS0Z,A0Z,A1Z,

& A2Z,A3Z,ICPZ

175 FORMAT(1X,3A4,T17,F9.3,T33,F9.6,T50,F9.6,T68,E12.5,T88,E12.5,

&T108,E12.5,T123,I1)

180 CONTINUE

WRITE(IWRT,184) T0,P0,MAXIT,CNMG,IDEBUG


```

184 FORMAT('0',/, '0', T10, 'THE ENTHALPY AND ENTROPY OF FORMATION ',
& 'REFERENCE TEMPERATURE AND PRESSURE ARE:', 5X, 'T0 = ', F6.1, ' K',
& 5X, 'P0 = ', F9.1, ' PA',/, '0', T35, 'MAXIMUM NUMBER OF ITERATIONS ',
& 'ALLOWED = ', I5,/, '0', T50, 'CONVERGENCE CRITERION = ', E12.4,
&/, '0', T48, 'OUTPUT PARAMETER IDEBUG = ', I2)
IF(S.GT.1) WRITE(IWRT,185) IXSCOR,AXS,BXS
185 FORMAT('0', 'EXCESS FREE ENERGY CORRELATION DATA :',
& 2X, 'IXSCOR = ', I5, 5X, 'AXS = ', E12.5, 5X, 'BXS = ', E12.5)
IF(ISS.GT.0) WRITE(IWRT,186) ISS
186 FORMAT('0', T24, 'ISS= ', I2, ' THE III-V LIQUID SOLUTION IS ',
& 'AT EQUILIBRIUM WITH THE III-V STOICHIOMETRIC SOLID')
187 CONTINUE
C
C THE TEMPERATURE AND PRESSURE LOOPS BEGIN HERE
C
DO 6000 ITP=1,NTP
IF(IOPT.EQ.1.AND.ITP.GT.1) T=T+TINC
IF(IOPT.EQ.2.AND.ITP.GT.1) P=P+PINC
IF(IOPT.EQ.4.AND.ITP.GT.1) T=T+TINC
IF(IOPT.EQ.5.AND.ITP.GT.1) P=P+PINC
C
C CALCULATE THE STANDARD STATE CHEMICAL POTENTIALS
C AND AN INITIAL ESTIMATE OF THE EQUILIBRIUM COMPOSITIONS
C
CALL STSTCP(A0,A1,A2,A3,A0Z,A1Z,A2Z,A3Z,DH0,DS0,DH0Z,DS0Z,STDCP,
& STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C,E,IDIM2,A,IREFAC,IX)
IF(ITP.GT.1.AND.ISS.EQ.0) GO TO 195
DO 190 I=1,VPS
FRAC(I)=FRACIN(I)
190 CONTINUE
FRACZ=FRCZIN
CALL ESTMTE(TOTMV,TOTMS,TOTMC,FRAC,N,FRACZ,ZV,IDIM1,V,S,C)
195 CONTINUE
C
C SOURCE ZONE STEADY-STATE LIQUID COMPOSITION MODEL
C
IF(ISS.GT.0) CALL STEADY(SPECIE,A,STDCP,ELMNT,XIII,T,T0,V,S,C,
& IDIM1,IDIM2,ISS,IWRT)
C
C CALCULATE THE TOTAL GRAM-MOLES OF EACH ELEMENT
C BASED ON THE INITIAL COMPOSITION ESTIMATES IN THE PHASES
C
C+++++
WRITE(IWRT,201)

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```

201 FORMAT(5X,'INITIAL ELEMENTAL ABUNDANCES')
  WRITE(IWRT,*) ''
  DO 200 J=1,E
    BCALC(J)=0.
  DO 210 I=1,VSC
    BCALC(J)=A(I,J)*N(I)+BCALC(J)
  B(J)=BCALC(J)
210 CONTINUE
  WRITE(IWRT,202) ELMNT(J),B(J)
202 FORMAT(3X,A2,2X,E12.5)
200 CONTINUE
  WRITE(IWRT,*) ''
  WRITE(IWRT,*) ''
  IF(IWRAP.GT.1) GO TO 476
  IF(ITP.GT.1) GO TO 472
C+++++
C
C WRITE-OUT THE INITIAL COMPOSITION ESTIMATES, STANDARD STATE
C CHEMICAL POTENTIALS AND THE ELEMENTAL ABUNDANCE MATRIX
C
  IPAGE=IPAGE+1
  WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
400 FORMAT('1','0',T34,'STOICHIOMETRIC FORMULATION FOR
DETERMINING',
& 'EQUILIBRIUM COMPOSITIONS','0',T30,20A4,T120,
& 'PAGE',I2)
  WRITE(IWRT,410) T,P
410 FORMAT('0',T43,'TEMPERATURE = ',F6.1,' K',5X,'PRESSURE = ',E12.5,
& ' PA')
  WRITE(IWRT,420) (ELMNT(K),K=1,13)
420 FORMAT('0',T48,'INPUT DATA AND INITIAL COMPOSITION ESTIMATES',
&','0',T29,'INITIAL',T43,'STANDARD',1X,T27,'COMPOSITION',
&T43,'CHEMICAL',1X,T4,'SPECIE',T29,'ESTIMATE',T42,'POTENTIAL',
&T72,'ELEMENTAL ABUNDANCE MATRIX',1X,T4,'SYMBOL',T17,'PHASE',
&T28,'(G-MOLES)',T40,'(KCAL/G-MOLE)',T55,13(A2,4X),'+',
&12('_',T15,9(_),T25,14(_),T40,13(_),T55,78(_))
  DO 440 I=1,VSC
    WRITE(IWRT,430) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),N(I),
& STDCP(I)
    IF(IEQ.V) WRITE(IWRT,430) (INERT(K),K=1,3),(PHASE(I,K),K=1,3),
& ZV,STDCPZ
430 FORMAT(1X,3A4,T15,3A3,T25,E14.7,T42,F9.3)
440 CONTINUE
  IF(ISS.GT.0) WRITE(IWRT,445) XIII

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445 FORMAT(4X,'X=',F6.4)
    WRITE(IWRT,450)
450 FORMAT('0',/, '0',T44,'TOTAL GRAM-MOLES OF EACH ELEMENT FROM IN',
&  'PUT DATA',/,1X,T40,'AND AS CALCULATED FROM THE INITIAL',
&  'COMPOSITION ESTIMATES',/, '0',4(4X,'INPUT DATA',3X,
&  'CALCULATED',5X))
    NPRT=E/4
    NCHK=NPRT*4
    IF(NCHK.NE.E) NPRT=NPRT+1
    ISTRT=1
    DO 470 K=1,NPRT
    NEND=ISTRT+3
    IF(NEND.GT.E) NEND=E
    WRITE(IWRT,460) (ELMNT(J),B(J),BCALC(J),J=ISTRT,NEND)
460 FORMAT(1X,4(A2,1X,E12.5,1X,E12.5,4X))
    ISTRT=NEND+1
470 CONTINUE
472 CONTINUE
    IPAGE=IPAGE+1
    WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
    WRITE(IWRT,410) T,P
    WRITE(IWRT,475)
475 FORMAT('0',T58,'EXECUTION DIAGNOSTICS',/, '+',T58,9(' '),1X,
&  11(' '),/, '0')
476 CONTINUE
C
C DIVIDE THE STANDARD STATE CHEMICAL POTENTIALS BY RT
C
    RT=0.0019872*T
    DO 480 I=1,VSC
    STDCP(I)=STDCP(I)/RT
480 CONTINUE
    STDCPZ=STDCPZ/RT
C
C CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR
C PHASE
C AND WRITE-OUT THE INITIAL RESULTS TO THE WRAPUP FILE
C
    IF(ITP.GT.1.OR.IWRAP.EQ.0) GO TO 485
    CALL TOTSI(A,ELMNT,FRAC,N,SITOT,SIMF,ACTSIS,T,P,IDIM1,IDIM2,V,E)
    CALL RATIO(A,ELMNT,FRAC,N,STDCP,ACTGAS,ACTINS,ACTASS,ACTPS,
&  RIIIV,RGAAS,RINP,T,P,T0,P0,IDIM1,IDIM2,V,E)
    ITBST=1
    BSTCVG=0

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```

CALL WRAPUP(TITLE,SPECIE,INERT,N,FRAC,QUES,ZV,FRACZ,SITOT,SMF,
& ACTSIS,ACTGAS,ACTINS,ACTPS,ACTASS,RIIV,RGAAS,RINP,
& BSTCVG,ITBST,CNVG,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,V,VSC,
& IOPT,ITP,NTP,ITAB,ICMP,IBL,ICOML,ICOMP1,ICOMP2)
485 CONTINUE
C
C ITERATIVE SOLUTION FOR THE EQUILIBRIUM COMPOSITIONS
C
C-----
C BEGIN NON-IDEAL LOOP
C
  IG1=1
  IGL1=1
  IGG1=1
  IG2=1
  INONI=0
  FS1=FRAC(27)
601 CALL
ACTCOF(FRAC,ACOE,ISPCE,SPECIE,INDEX,IDIM1,RELMAX,IXSCOR,
& AXS,BXS,T,IACFF,V,S,C,IWRT,FS1)
  IDX1=INDEX(1)
  IDX2=INDEX(2)
  INONI=INONI+1
  DMFI=FS1
  STDCP(IDX1)=0.8/RT
  GAM=ACOE(FIDX1)
  STDCP(IDX1)=STDCP(IDX1)+DLOG(GAM)
  ACOE(FIDX1)=1.0D+00
  STDCP(IDX2)=(33.1-(3.5E-03)*T)/RT
  GAM=ACOE(FIDX2)
  STDCP(IDX2)=STDCP(IDX2)+DLOG(GAM)
  ACOE(FIDX2)=1.0D+00
C-----
  ITO=500
C-----
  RELMAX=1.0E10
  IACFF=0
  DO 600 ITER=1,MAXIT
C-----
    IF(ITER.EQ.ITO) WRITE(*,*) ' ITER= ',ITER
    IF(ITER.EQ.ITO) ITO=ITO+500
C-----
C
C DETERMINE THE OPTIMUM SET OF BASIS SPECIES

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C
  CALL OPTBAS(N,BESTN,A,D,DPRME,STDCP,SPECIE,PHASE,A0,A1,A2,A3,
    &BQUES,DH0,DS0,ICP,IDXBAS,ITER,IDIM1,IDIM2,V,S,C,E,ISTOP,ICHNG,
    &IWRT,FRAC)
  IF(ISTOP.EQ.1) GO TO 604
  IF(ITER.GT.1.AND.ICHNG.EQ.0) GO TO 500
  IF(IDEBUG.LT.2) GO TO 490
  CALL IPVEC(IDXBAS,IDIM2,E,6HIDXBAS,IWRT)
  CALL PMAT(A,IDIM1,IDIM2,VSC,E,6HA ,IWRT)
  CALL PMAT(D,IDIM2,IDIM2,E,E,6HD ,IWRT)
  CALL DPMAT(DPRME,IDIM2,IDIM2,E,E,6HDPME ,IWRT)
490 CONTINUE
C
C CALCULATE THE STOICHIOMETRIC COEFFICIENTS AND THE EQUILIBRIUM
C CONSTANTS
C
  CALL EQCON(A,D,DD,DINV,DG,GNU,STDCP,KEQ,IDXBAS,WKA,
    & IDIM1,IDIM2,V,S,C,E,ISTOP)
  IF(ISTOP.EQ.1) GO TO 604
  IF(IDEBUG.LT.2) GO TO 500
  CALL DPMAT(DINV,IDIM2,IDIM2,E,E,6HDINV ,IWRT)
  CALL PMAT(GNU,IDIM1,IDIM2,VSC,E,6HGNU ,IWRT)
  CALL PVEC(KEQ,IDIM1,VSC,6HKEQ ,IWRT)
500 CONTINUE
C
C CALCULATE THE EQUILIBRIUM CONSTANTS FROM THE CURRENT
COMPOSITIONS
C
  CALL CALCQ(GNU,N,ACOE,FRAC,PHASE,VAPOR,SOLN,IDXBAS,Q,
    & ZV,FRACZ,P,P0,V,S,C,E,IDIM1,IDIM2)
C
C CALCULATE THE ERROR BETWEEN THE EQUILIBRIUM CONSTANTS
C CALCULATED BY THE COMPOSITIONS AND THE EQUILIBRIUM
CONSTANTS
C
C CALCULATED FROM THE GIBBS FREE ENERGY CHANGE
C
  RELMAX=0.
  DO 590 I=1,VSC
  QUES(I)=BLNKS
  DO 570 J=1,E
  IF(1.EQ.IDXBAS(J)) GO TO 590
570 CONTINUE
  RELERR=(-1.0)*RT*DG(I)+RT*DLOG(Q(I))
C

```

C ASSIGN "?" TO QUES(I) IF THE CONVERGENCE CRITERION IS NOT MET
 C AND "???" TO QUES(I) IF THERE IS LESS THAN ONE SIGNIFICANT FIGURE

C

```
IF(ABS(RELERR).GT.CNVG) QUES(I)=QUEST1
IF(ABS(RELERR).GT.0.001) QUES(I)=QUEST2
IF(ABS(RELERR).GT.RELMAX.AND.N(I).GE.1.0D-50)
&      RELMAX=ABS(RELERR)
```

590 CONTINUE

C

C KEEP THE BEST ESTIMATE TO THE EQUILIBRIUM SOLUTION
 C IN CASE THE NUMERICAL PROCEDURE DIVERGES

C

```
IF(ITER.GT.1.AND.RELMAX.GT.BSTCVG) GO TO 594
BSTCVG=RELMAX
ITBST=ITER
DO 593 IBEST=1,VSC
BQUES(IBEST)=QUES(IBEST)
BESTN(IBEST)=N(IBEST)
```

593 CONTINUE

594 CONTINUE

```
IF(RELMAX.LE.CNVG) GO TO 610
IF(IDEBUG.EQ.2) CALL PVEC(FRAC,IDIM1,VSC,6HFRAC ,IWRT)
IF(IDEBUG.GE.1) CALL PVEC(Q,IDIM1,VSC,6HQ ,IWRT)
IF(ITER.EQ.MAXIT) GO TO 595
```

C

C MAKE ADJUSTMENTS TO THE EXTENTS OF REACTION

C

```
CALL ADJEXT(N,Q,GNU,DZETA,IDXBAS,COND,PHASE,IDIM1,IDIM2,
&      V,S,C,E,DG,VAPOR,SOLN)
CALL CNVFRC(N,NTEMP,STDCP,ACOE,DZETA,GNU,IDXBAS,VAPOR,
&SOLN,PHASE,ZV,RT,P,P0,RLXMIN,LAMBDA,IDIM1,IDIM2,V,S,C,E)
CALL CORMOL(N,DZETA,GNU,IDXBAS,IDIM1,IDIM2,LAMBDA,VSC,E)
```

595 IF(ITER.LT.MAXIT) GO TO 597

C

C IF THE SOLUTION DID NOT CONVERGE TRANSFER THE BEST ESTIMATE
 C TO THE EQUILIBRIUM SOLUTION FROM VECTOR BESTN INTO N.

C

```
DO 596 IBEST=1,VSC
QUES(IBEST)=BQUES(IBEST)
N(IBEST)=BESTN(IBEST)
```

596 CONTINUE

597 CONTINUE

```
CALL CALCQ(GNU,N,ACOE,FRAC,PHASE,VAPOR,SOLN,IDXBAS,Q,
&      ZV,FRACZ,P,P0,V,S,C,E,IDIM1,IDIM2)
```

```

      IF(IDEBUG.EQ.0) GO TO 600
      CALL
GIBBS(N,STDCP,STDCPZ,ACOE,FRAC,ZV,FRACZ,COND,SOLN,PHASE,
      &      RT,P,P0,IDIM1,V,S,C,GFE)
C+++++
      IF(ITER.EQ.1) IGFE=100
      IF(ITER.EQ.IGFE.OR.ITER.EQ.MAXIT) THEN
        WRITE(IWRT,540) ITER,GFE
540 FORMAT(1X,'ITER=',3X,I5,5X,'TOTGIBBS=',3X,E12.5)
        IGFE=IGFE+100
        ELSE
        GO TO 541
        ENDIF
541 CONTINUE
C+++++
      CALL DEBUG(N,DZETA,VSC,IDIM1,ITER,LAMBDA,GFE,RELMAX,IWRT)
600 CONTINUE
604 CONTINUE
      IF(IWRAP.LT.3) WRITE(IWRT,605)MAXIT,RELMAX,BSTCVG,ITBST
605 FORMAT('0','***** ITERATION FOR EQUILIBRIUM COMPOSITION ',
      &      'DID NOT CONVERGE *****',
      &      ' (AFTER ',I4,' ITERATIONS RELMAX =',E12.5,')',
      &      '/,0,' BEST CONVERGENCE=',E12.5,' AT ITERATION ',I4)
610 CONTINUE
C-----
C END OF NON-IDEAL LOOP
C
      DO 607 JID=1,S
      KID=V+JID
      DO 607 IID=1, VSC
      IF(SPECIE(IID,1).EQ.ISPCE(KID,1).AND.
      & SPECIE(IID,2).EQ.ISPCE(KID,2).AND.
      & SPECIE(IID,3).EQ.ISPCE(KID,3)) INDEX(JID)=IID
607 CONTINUE
      IDX1=INDEX(1)
      IDX2=INDEX(2)
      DMFF=FRAC(IDX1)
602 ERRDMF=DMFF-DMFI
      IF(DABS(ERRDMF).GE.1E-07.AND.IG1.EQ.1)THEN
      IF(DMFF.LT.DMFI)THEN
        FS1=DMFI-1.0D-02
        IGL1=0
        IG3=1
        IF(IGL1.EQ.0.AND.IGG1.EQ.0) IG1=0

```

```

      IF(IGL1.EQ.0.AND.IGG1.EQ.0) GO TO 602
      ELSEIF(DMFF.GT.DMFI)THEN
        FS1=DMFI+1.0D-02
        IGG1=0
        IG3=2
        IF(IGL1.EQ.0.AND.IGG1.EQ.0) IG1=0
        IF(IGL1.EQ.0.AND.IGG1.EQ.0) GO TO 602
      ELSE
        ENDIF
      GO TO 601
    ELSEIF(ABS(ERRDMF).GE.1E-07.AND.IG1.EQ.0.AND.IG2.EQ.1)THEN
      IF(IG2.EQ.1.AND.IG3.EQ.1) DMFLO=FS1
      IF(IG2.EQ.1.AND.IG3.EQ.1) DMFHI=DMFI
      IF(IG2.EQ.1.AND.IG3.EQ.2) DMFLO=DMFI
      IF(IG2.EQ.1.AND.IG3.EQ.2) DMFHI=FS1
      IG2=0
      FS1=(DMFLO+DMFHI)/2.0
      GO TO 601
    ELSEIF(ABS(ERRDMF).GE.1E-07.AND.IG2.EQ.0)THEN
      IF(DMFF.LT.DMFI)THEN
        DMFHI=DMFI
        FS1=(DMFLO+DMFHI)/2.0
      ELSEIF(DMFF.GT.DMFI)THEN
        DMFLO=DMFI
        FS1=(DMFLO+DMFHI)/2.0
      ELSE
        ENDIF
      GO TO 601
    ELSE
      ERRDMF=DABS(ERRDMF)
      WRITE(*,606) INON1,ERRDMF
606 FORMAT(' NON-IDEAL LOOPS= ',I5,X,'ERROR= ',E12.5)
      ENDIF

```

```

C-----
C+++++
DO 572 J=1,E
K=IDXBAS(J)
DO 573 L=1,3
BASIS(J,L)=SPECIE(K,L)
573 CONTINUE
572 CONTINUE
C+++++
WRITE(IWRT,540) ITER,GFE
WRITE(IWRT,*)

```



```

WRITE(IWRT,*)
WRITE(IWRT,569) T,ITER-1
569 FORMAT(2X,'TEMP=',2X,F8.2,5X,'# ITER=',3X,I5)
C+++++
DO 574 I=1,VSC
DO 575 J=1,E
IF(LEQ.IDXBAS(J)) GO TO 574
575 CONTINUE
WRITE(IWRT,576) (GNU(I,J),(BASIS(J,K),K=1,3),J=1,E)
576 FORMAT(4(F5.2,3A4,1X))
F1=(-1.0)*RT*DG(I)
F2=RT*DLOG(Q(I))
FREE=(-1.0)*RT*DG(I)+RT*DLOG(Q(I))
WRITE(IWRT,577) (SPECIE(I,L),L=1,3),F1,F2,FREE
577 FORMAT(1X,3A4,3(3X,E12.5))
WRITE(IWRT,*) ''
574 CONTINUE
WRITE(IWRT,*) ''
WRITE(IWRT,701)
701 FORMAT(5X,'FINAL ELEMENTAL ABUNDANCES AND DIFFERENCE (B-
&B*)')
DO 702 J=1,E
BCALC(J)=0.
DO 703 I=1,VSC
BCALC(J)=A(I,J)*N(I)+BCALC(J)
703 CONTINUE
B(J)=B(J)-BCALC(J)
WRITE(IWRT,704) ELMNT(J),BCALC(J),B(J)
704 FORMAT(3X,A2,2(2X,E12.5))
702 CONTINUE
WRITE(IWRT,*) ''
WRITE(IWRT,*) ''
C+++++
CALL
GIBBS(N,STDCP,STDCPZ,ACOE,FRAC,ZV,FRACZ,COND,SOLN,PHASE,
& RT,P,P0,IDIM1,V,S,C,GFE)
C
C CALCULATE THE GRAM-MOLES OF EACH ELEMENT AFTER THE
C ITERATIONS
C
DO 700 J=1,E
BCALC(J)=0.0
DO 700 I=1,VSC
BCALC(J)=BCALC(J)+A(I,J)*N(I)

```

700 CONTINUE

C+++++

C

C CALCULATE THE CHEMICAL POTENTIAL OF EACH SPECIE

C

WRITE(IWRT,*) ' SPECIES ST. ST. CHEM. POT. (KJ/MOL) CH
&EM. POT. (KJ/MOL)'

WRITE(IWRT,*) ''

DO 800 I=1,VSC+IX

PP0=1.0

IF(PHASE(I,1).EQ.VAPOR(1)) PP0=P/P0

ARG=FRAC(I)*ACOE(I)*PP0

IF(I.GT.VSC) ARG=1.0

CHMPT(I)=RT*(STDCP(I)+DLOG(ARG))

IF(I.GT.VSC) CHMPT(I)=STDCP(I)

STP=4.184*RT*STDCP(I)

CHM=4.184*CHMPT(I)

WRITE(IWRT,801) (SPECIE(I,J),J=1,3),STP,CHM

801 FORMAT(2X,3A4,12X,F12.5,15X,F12.5)

800 CONTINUE

WRITE(IWRT,*) ''

WRITE(IWRT,*) '-----'

WRITE(IWRT,*) ''

WRITE(IWRT,*) ''

ARG=1.0

IF(FRACZ.GT.0.0) ARG=FRACZ*P/P0

CHMPTZ=RT*(STDCPZ+ALOG(ARG))

DO 810 I=1,VSC

DO 810 K=1,3

BSPCE(I,K)=SPECIE(I,K)

810 CONTINUE

C+++++

C

C PUT THE MATRICIES AND VECTORS INTO THE ORIGINAL PROBLEM
STATEMENT ORDER

C

CALL ORDER(ISPCE,SPECIE,PHASE,N,A,STDCP,A0,A1,A2,A3,DH0,DS0,
&DZETA,CHMPT,ACOE,FRAC,QUES,DG,Q,KEQ,ICP,IDIM1,IDIM2,E,VSC)

C-----

BMOLE=FRAC(IB)

C-----

C

C CALCULATE THE TOTAL SILICON AND THE III/V RATIO IN THE VAPOR
PHASE

```

C
  CALL TOTS1(A,ELMNT,FRAC,N,SITOT,SIMF,ACTSIS,T,P,IDIM1,IDIM2,V,E)
  CALL RATIO(A,ELMNT,FRAC,N,STDCP,ACTGAS,ACTINS,ACTASS,ACTPS,
    &      RIIV,RGAAS,RINP,T,P,T0,P0,IDIM1,IDIM2,V,E)
  IF(IWRAP.GT.1) GO TO 971
C
C WRITE-OUT THE RESULTS
C
  IPAGE=IPAGE+1
  WRITE(IWRT,400) (TITLE(K),K=1,20),IPAGE
  WRITE(IWRT,410) T,P
  WRITE(IWRT,900) ITBST,GFE,BSTCVG,CNVG,LAMBDA
900 FORMAT('0',/,'1X,T45,'EQUILIBRIUM COMPOSITIONS AFTER ',I5,
  & ' ITERATIONS',/,'0',T42,'SYSTEM GIBBS FREE ENERGY = ',E14.7,
  & ' (KCAL)',
  & /,'0','RELATIVE ERROR = ',E12.5,5X,'CONVERGENCE CRITERION = ',
  & E12.5,5X,'RELAXATION PARAMETER AT LAST ITERATION = ',E12.5,
  & /,'0',T57,'ESTIMATED',/,'1X,T25,'EQUILIBRIUM',T39,'EQUILIBRIUM',
  & T56,'COMPOSITION',T92,'CHEMICAL',
  & /,'1X,T4,'SPECIE',T29,'MOLE',T39,'COMPOSITION',T56,
  & 'UNCERTAINTY',T91,'POTENTIAL',T109,'ACTIVITY',
  & /,'1X,T4,'SYMBOL',T17,'PHASE',T27,'FRACTION',T40,'(G-MOLES)',
  & T57,'(G-MOLES)',T90,'(KCAL/G-MOLE)',T107,'COEFFICIENT',
  & /,'+',I2(' '),T15,9(' '),T25,I2(' '),T37,I4(' '),T54,
  & I4(' '),T89,I4(' '),T106,I2(' '))
  ZZETA=0.0
  ZACT=1.0
  DO 920 I=1,VSC
  WRITE(IWRT,910) (SPECIE(I,K),K=1,3),(PHASE(I,K),K=1,3),FRAC(I),
  &      N(I),DZETA(I),CHMPT(I),ACOE(I)
  IF(IEQ.V) WRITE(IWRT,910) (INERT(K),K=1,3),(PHASE(I,K),K=1,3),
  &      FRACZ,ZV,ZZETA,CHMPTZ,ZACT
910 FORMAT(1X,3A4,T15,3A3,T24,E12.5,T37,E14.7,T54,E14.7,T92,F9.3,
  & T106,E12.5)
920 CONTINUE
  IF(ISS.GT.0) WRITE(IWRT,445) XIII
  WRITE(IWRT,930) SIMF
930 FORMAT('0',T35,'MOLE FRACTION OF SILICON SPECIES IN ',
  & 'VAPOR PHASE = ',E12.5)
  WRITE(IWRT,940) RIIV
940 FORMAT('0',T50,'III/V RATIO IN THE VAPOR PHASE = ',E9.4)
  WRITE(IWRT,950)
950 FORMAT('0',/,'0',T44,'TOTAL GRAM-MOLES OF EACH ELEMENT FROM IN',
  & 'PUT DATA',/,'1X,T42,'AND AS CALCULATED FROM THE EQUILIBRIUM',

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```

&  ' COMPOSITIONS',/,0',4(4X,'INPUT DATA',3X,
&  'CALCULATED',5X))
NPRT=E/4
NCHK=NPRT*4
IF(NCHK.NE.E) NPRT=NPRT+1
ISTRT=1
DO 970 K=1,NPRT
NEND=ISTRT+3
IF(NEND.GT.E) NEND=E
WRITE(IWRT,960) (ELMNT(J),B(J),BCALC(J),J=ISTRT,NEND)
960 FORMAT(1X,4(A2,1X,E12.5,1X,E12.5,4X))
ISTRT=NEND+1
970 CONTINUE
971 CONTINUE
IF(IWRAP.GT.0)CALL
WRAPUP(TITLE,SPECIE,INERT,N,FRAC,QUES,ZV,FRACZ,
&SITOT,SIMF,ACTSIS,ACTGAS,ACTINS,ACTPS,ACTASS,RMIIV,RGAAS,RINP,
&BSTCVG,ITBST,RELMAX,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,V,VSC,
&IOPT,ITP,NTP,ITAB,ICMP,IBL,ICOML,ICOMP1,ICOMP2)
IF(ITP.GT.1.OR.ICMP.GT.1.OR.IWRAP.GT.1) GO TO 1900
C
C WRITE-OUT THE INDEPENDENT REACTION EQUATIONS
C
IPAGE=IPAGE+1
WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE
WRITE(IWRT,410) T,P
WRITE(IWRT,980)
980 FORMAT('0',T34,'A SET OF INDEPENDENT REACTION EQUATIONS FOR ',
&  'THIS SYSTEM IS AS FOLLOWS:',/,0')
DO 1100 I=1,VSC
C
C DETERMINE THE NUMBER OF BASIS SPECIES IN EACH FORMATION
CREACTION
C
NSPEC=0
DO 990 K=1,E
IF(LEQ.IDXBAS(K)) GO TO 1100
IF(ABS(GNU(I,K)).LT.1.0E-6) GO TO 990
NSPEC=NSPEC+1
990 CONTINUE
C
C FILL THE CHARACTER ARRAY "STRING" WITH THE FORMATION
CREACTION SPECIES
C

```

```

NLOOP=1
IF(NSPEC.GT.4) NLOOP=FLOAT(NSPEC)/4.0+0.9
DO 1000 K=1,3
  STRING(1,K)=BSPCE(I,K)
1000 CONTINUE
  STRING(1,4)=RPAS
  COEFF(1)=1.0
  IST=1
  ICNT=0
  DO 1060 ILOOP=1,NLOOP
    NCNT=NSPEC-ICNT+1
    IF(NCNT.GT.5) NCNT=5
    DO 1020 IDX=2,NCNT
      ICNT=ICNT+1
      DO 1015 IBASE=IST,E
        IF(ABS(GNU(I,IBASE)).LT.1.0E-6) GO TO 1015
        IDXB=IDXBAS(IBASE)
        DO 1010 K=1,3
          STRING(IDX,K)=BSPCE(IDXB,K)
1010 CONTINUE
          COEFF(IDX)=GNU(I,IBASE)
          STRING(IDX,4)=RPSPS
          GO TO 1018
1015 CONTINUE
1018 IST=IBASE+1
1020 CONTINUE
      STRING(NCNT,4)=RPBL
      IF(ILOOP.EQ.1) WRITE(IWRT,1040)(LP,COEFF(IJK),
        & (STRING(IJK,K),K=1,4),IJK=1,NCNT)
1040 FORMAT('0',A1,F5.2,4A4,4(A1,E10.3,4A4))
      IF(ILOOP.GT.1) WRITE(IWRT,1050) SSPS,(LP,COEFF(IJK),
        & (STRING(IJK,K),K=1,4),IJK=2,NCNT)
1050 FORMAT(1X,T20,A4,4(A1,E10.3,4A4))
1060 CONTINUE
1100 CONTINUE
C
C WRITE-OUT A COMPARISON BETWEEN THE EQUILIBRIUM CONSTANTS
C AS CALCULATED BY THE GIBBS FREE ENERGY CHANGE AND BY
C COMPOSITION
C
  IPAGE=IPAGE+1
  WRITE(IWRT,400) (TITLE(K),K=1,20), IPAGE
  WRITE(IWRT,410) T,P
  WRITE(IWRT,1110)

```

```

1110 FORMAT('0',1X,T40,'EQUILIBRIUM CONSTANTS FOR THE
&INDEPENDENT',
  &' REACTIONS',/, '0',T20,'GIBBS FREE ENERGY CHANGE',T47,
  &'EQUILIBRIUM CONSTANT',T73,'EQUILIBRIUM CONSTANT',/,1X,
  &'REACTION PRODUCT',T25,'(KCAL/G-MOLE)',T46,'FROM GIBBS FREE ',
  &'ENERGY',T70,'FROM PREDICTED COMPOSITION',/, '+',16('_',),T20,
  &24('_',),T46,22('_',),T70,26('_',))
DO 1200 I=1,VSC
  IF(N(I).GT.1.00E-21) WRITE(IWRT,1120) (SPECIE(I,K),K=1,3),DG(I),
  & KEQ(I),Q(I)
  IF(N(I).LE.1.00E-21) WRITE(IWRT,1121) (SPECIE(I,K),K=1,3),DG(I),
  & KEQ(I),Q(I)
1120 FORMAT(1X,3A4,T28,F8.3,T51,E12.5,T77,E12.5)
1121 FORMAT(1X,3A4,T28,F8.3,T51,E12.5,T77,E12.5,2X,'(NOT BINDING)')
1200 CONTINUE
  IF(ISS.GT.0) WRITE(IWRT,445) XIII
1900 IF(ISTOP.EQ.1) GO TO 3000
C-----
6000 CONTINUE
C-----
C
C CHANGE MOLE FRACTIONS OF INLET GAS TO FIND CVD DIAGRAM
BOUNDARIES
C
  IF(ICOML.LT.2) GO TO 2300
  IF(ICU.EQ.1) THEN
    IF(BMOLE.LT.FRACLIM.AND.I1.EQ.0)THEN
      IF(I2.EQ.0)THEN
        I2=1
        FRACON=FRACIN(ISPLL)
        FF=FRACIN(ISPLL)/2.0
        FRACIN(ISPLL)=FRACIN(ISPLL)+SFF*FF
      ELSE
        I2=0
        FRACON=FRACIN(ISPLL)
        FF=FRACIN(ISPLL)*0.8
        FRACIN(ISPLL)=FRACIN(ISPLL)+SFF*FF
      ENDIF
      GO TO 2200
    ELSEIF(BMOLE.LT.FRACLIM.AND.I1.EQ.1)THEN
      FRACON=FRACIN(ISPLL)
      FF=(FRACIN(ISPLL)-FRACBASE)/2.0
      IF(FF.LT.0.0) FF=-1.0*FF
      FRACIN(ISPLL)=FRACIN(ISPLL)+SFF*FF
    
```

```

    FRACRA=(FRACON-FRACIN(ISPLL))/FRACERR
    IF(DABS(FRACRA).LE.FRACCU) I1=2
    GO TO 2200
ELSEIF(BMOLE.GE.FRACLIM.AND.I1.LT.2)THEN
    IF(I2.EQ.0.AND.I1.EQ.0) FRACERR=FRACON/5.0
    IF(I2.EQ.1.AND.I1.EQ.0) FRACERR=FRACON/10.0
    I1=1
    FRACBASE=FRACIN(ISPLL)
    FRACRA=(FRACON-FRACIN(ISPLL))/FRACERR
    IF(DABS(FRACRA).LE.FRACCU) I1=2
    FF=(FRACON-FRACIN(ISPLL))/2.0
    IF(FF.LT.0.0) FF=-1.0*FF
    FRACIN(ISPLL)=FRACON+SFF*FF
    GO TO 2200
ELSE
    GO TO 2300
ENDIF
ELSE
    IF(BMOLE.LT.FRACLIM.AND.I1.EQ.0)THEN
        FRACON=FRACIN(ISPLL)
        CHKNEG=FRACIN(ISPLL)+SFF*FF
        IF(CHKNEG.LT.CLOOP1) CLOOP1=0.1*CLOOP1
        FF=CLOOP1
        FRACIN(ISPLL)=FRACIN(ISPLL)+SFF*FF
        GO TO 2200
    ELSEIF(BMOLE.LT.FRACLIM.AND.I1.EQ.1)THEN
        FRACON=FRACIN(ISPLL)
        FF=(FRACIN(ISPLL)-FRACBASE)/2.0
        IF(FF.LT.0.0) FF=-1.0*FF
        FRACIN(ISPLL)=FRACIN(ISPLL)+SFF*FF
        FRACRA=(FRACON-FRACIN(ISPLL))/FRACERR
        IF(DABS(FRACRA).LE.FRACCU) I1=2
        GO TO 2200
    ELSEIF(BMOLE.GE.FRACLIM.AND.I1.LT.2)THEN
        IF(FRACON.LT.1.0E+00.AND.FRACON.GE.1.0E-01) FRACERR=1.0E-01
        IF(FRACON.LT.1.0E-01.AND.FRACON.GE.1.0E-02) FRACERR=1.0E-02
        IF(FRACON.LT.1.0E-02.AND.FRACON.GE.1.0E-03) FRACERR=1.0E-03
        IF(FRACON.LT.1.0E-03.AND.FRACON.GE.1.0E-04) FRACERR=1.0E-04
        IF(FRACON.LT.1.0E-04.AND.FRACON.GE.1.0E-05) FRACERR=1.0E-05
        IF(FRACON.LT.1.0E-05.AND.FRACON.GE.1.0E-06) FRACERR=1.0E-06
        I1=1
        FRACBASE=FRACIN(ISPLL)
        FRACRA=(FRACON-FRACIN(ISPLL))/FRACERR
        IF(DABS(FRACRA).LE.FRACCU) I1=2

```

```

      FF=(FRACON-FRACIN(ISPLL))/2.0
      IF(FF.LT.0.0) FF=-1.0*FF
      FRACIN(ISPLL)=FRACON+SFF*FF
      GO TO 2200
    ELSE
      GO TO 2300
    ENDIF
  ENDIF
2300 IF(ICOML.GE.2.AND.IWRAP.EQ.7) WRITE(IFILE,2301) FRACIN(ISP1),
&                                     FRACIN(ISP2)
2301 FORMAT(1X,E10.3,3X,E10.3)
      CTI=FRAC(28)/FRAC(27)
      IF(ICOML.LE.1.AND.IWRAP.EQ.8) WRITE(IFILE,2302) FRACIN(ISP2),
&                                     FRACIN(ISP1),CTI
2302 FORMAT(1X,E10.3,3X,E10.3,3X,F10.5)

C-----
5400 CONTINUE
5300 CONTINUE
5200 CONTINUE
5100 CONTINUE
C-----
      IF(JTBOU.NE.NTBOU)GO TO 7000
C-----
2000 CONTINUE
3000 IF(IWRAP.LT.7) WRITE(IWRT,3001)
3001 FORMAT('1,')
      IF(IOPT.EQ.0.OR.IOPT.EQ.3)
&      CALL SPECIL(N,A,E,V,S,SPECIE,ELMNT,IFILE)
4002 STOP
      END
      SUBROUTINE STSTCP(A0,A1,A2,A3,A0Z,A1Z,A2Z,A3Z,DH0,DS0,DH0Z,DS0Z,
&      STDCP,STDCPZ,ICP,ICPZ,T0,T,IDIM1,V,S,C,E,IDIM2,A,IREAC,IX)
C
C THIS SUBROUTINE CALCULATES THE STANDARD STATE CHEMICAL
POTENTIALS
C REFERENCE STATE: PURE COMPONENT (APPROPRIATE PHASE)
C      AT TEMPERATURE T AND PRESSURE P0.
C
      DIMENSION A0(IDIM1),A1(IDIM1),A2(IDIM1),A3(IDIM1),DH0(IDIM1),
&      DS0(IDIM1),STDCP(IDIM1),ICP(IDIM1),IREAC(IDIM2),
&      A(IDIM1,IDIM2)
      INTEGER V,S,C,VSC,E
      VSC=V+S+C

```



```

DT=T-T0
DT2=T**2-T0**2
DT3=T**3-T0**3
DT4=T**4-T0**4
DTM1=1.0/T-1.0/T0
DTM2=1.0/T/T-1.0/T0/T0
DLNT=ALOG(T)-ALOG(T0)
DLNT2=ALOG(T)**2-ALOG(T0)**2
DTLNT=T*ALOG(T)-T0*ALOG(T0)

```

C

C CHEMICAL POTENTIALS FOR THE VAPOR, SOLUTION AND CONDENSED PHASES

C

```

DO 100 I=1,VSC+IX
DELH=A0(I)*DT+A1(I)*DT2/2.-A2(I)*DTM1+A3(I)*(DTLNT-DT)
DELS=A0(I)*DLNT+A1(I)*DT-A2(I)*DTM2/2.+A3(I)*DLNT2/2.
IF(ICP(I).EQ.1) DELH=A0(I)*DT+A1(I)*DT2/2.+A2(I)*DT3/3.
&      +A3(I)*DT4/4.
IF(ICP(I).EQ.1) DELS=A0(I)*DLNT+A1(I)*DT+A2(I)*DT2/2.
&      +A3(I)*DT3/3.
IF(ICP(I).EQ.2) DELH=A0(I)*DT+A1(I)*DT2/2.+A2(I)*DT3/3.
&      -A3(I)*DTM1
IF(ICP(I).EQ.2) DELS=A0(I)*DLNT+A1(I)*DT+A2(I)*DT2/2.
&      -A3(I)*DTM2/2.

```

C

C

C SOLUTION MODEL

C

C

```

IF(ICP(I).EQ.9)THEN
X1=1.0/(1.0+A(1,3))
X2=1.0-X1
R=1.987
AA0=-171340.0
BB0=27.243
AA1=-57886.0
BB1=11.877
AA2=499502.0
BB2=-176.677
AA3=450862.0
BB3=-237.296
C0=AA0+BB0*T
C1=AA1+BB1*T
C2=AA2+BB2*T

```

C3=AA3+BB3*T

C-----

DX=2.0*X1-1.0D+00

POLG=C0+C1*DX+C2*DX**2+C3*DX**3

DPOLG=2.0*C1+4.0*C2*DX+6.0*C3*DX**2

GAM1=EXP(((1.0-X1)**2)*(POLG+X1*DPOLG))/(R*T))

GAM2=EXP((X1**2)*(POLG-(1.0D+00-X1)*DPOLG))/(R*T))

ACT1=GAM1*X1

ACT2=GAM2*(1.0-X1)

C-----

UOTI=800.0

UOC=33100.0-3.5*T

UTI=UOTI+R*T*LOG(ACT1)

UC=UOC+R*T*LOG(ACT2)

STDCP(I)=(X1*UTI+X2*UC)/1000.0

ELSE

STDCP(I)=DH0(I)+DELH-T*(DS0(I)+DELS)

ENDIF

100 CONTINUE

C

C IDENTIFY REFERENCE SPECIES

C

DO 200 I=1,E

DO 300 J=1,VSC+IX

IF(DH0(J).NE.0.0.OR.A(J,I).EQ.0.0.OR.ICP(J).EQ.9) GO TO 300

IREAC(I)=J

GO TO 200

300 CONTINUE

200 CONTINUE

C

C CORRECT STANDARD STATE CHEM. POT. FOR ALL NON-REFERENCE
CSPECIES

C

DO 400 I=1,VSC+IX

DO 500 J=1,E

K=IREAC(J)

IF(K.EQ.I.OR.ICP(I).EQ.9) GO TO 400

STDCP(I)=STDCP(I)-(A(I,J)/A(K,J))*STDCP(K)

500 CONTINUE

400 CONTINUE

C

C CORRECT STANDARD STATE CHEM. POT. FOR THE REFERENCE SPECIES

C

DO 600 I=1,E

```

      K=IREAC(I)
      STDCP(K)=0.0
600 CONTINUE
C
C INERT CHEMICAL POTENTIAL
C
      DELH=A0Z*DT+A1Z*DT2/2.-A2Z*DTM1+A3Z*(DTLNT-DT)
      DELS=A0Z*DLNT+A1Z*DT-A2Z*DTM2/2.+A3Z*DLNT2/2.
      IF(ICPZ.EQ.1) DELH=A0Z*DT+A1Z*DT2/2.+A2Z*DT3/3.
      &      +A3Z*DT4/4.
      IF(ICPZ.EQ.1) DELS=A0Z*DLNT+A1Z*DT+A2Z*DT2/2.
      &      +A3Z*DT3/3.
      STDCPZ=DH0Z+DELH-T*(DS0Z+DELS)
      RETURN
      END
      SUBROUTINE
ESTMTE(TOTMV,TOTMS,TOTMC,FRAC,N,FRACZ,ZV,IDIM1,V,S,C)
C
C THIS SUBROUTINE CALCULATES AN INITIAL ESTIMATE
C TO THE SYSTEM EQUILIBRIUM COMPOSITIONS
C
      DIMENSION TOTMC(IDIM1)
      INTEGER V,S,C,VS,VS1,VSC
      REAL*8 N(IDIM1),FRAC(IDIM1)
      VS=V+S
      VS1=VS+1
      VSC=V+S+C
      TOTMOL=TOTMV
      DO 50 I=1,VS
      IF(I.GT.V) TOTMOL=TOTMS
      N(I)=TOTMOL*FRAC(I)
50 CONTINUE
      ZV=FRACZ*TOTMV
      IF(C.EQ.0) RETURN
      DO 60 I=VS1,VSC
      N(I)=TOTMC(I)
60 CONTINUE
      RETURN
      END
      SUBROUTINE STEADY(SPECIE,A,STDCP,ELMNT,XIII,T,T0,V,S,C,IDIM1,
      &      IDIM2,ISS,IWRT)
C
C SUBROUTINE TO CALCULATE THE SOLID-LIQUID EQUILIBRIUM
CCOMPOSITIONS

```

C FOR USE IN THE STEADY-STATE APPROXIMATION IN THE SOURCE ZONE

C

C ISS SYSTEM

C 1 GA(L)-AS(L)/GA-AS (S)

C 2 IN(L)-P(L)/IN-P (S)

C

DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1)

INTEGER SPECIE(IDIM1,3),ELMNT(IDIM2),IIIEL(2),VEL(2),V,S,C,VSC,

& LAST/'1-X)/',GA/'GA'/,AS/'AS'/,IN/'IN'/,P/'P'/

DATA IIIEL(1)/' GAX'/,IIIEL(2)/' INX'/,

& VEL(1)/'-AS('/,VEL(2)/'- P('/

THETA2(XV)=(TMIII*DSIIIV-AXS*(0.5-XV**2-(1.-XV)**2))/

& (DSIIIV-R*ALOG(4.*XV*(1.-XV))+BXS*(0.5-XV**2-(1.-XV)**2))

VSC=V+S+C

SPECIE(VSC,1)=IIIEL(ISS)

SPECIE(VSC,2)=VEL(ISS)

SPECIE(VSC,3)=LAST

DT=T-T0

DT2=T**2-T0**2

DTM1=1.0/T-1.0/T0

DTM2=1.0/T**2-1.0/T0**2

DLNT=ALOG(T/T0)

IF(ISS.EQ.2) GO TO 50

C

C GA-AS SYSTEM

C

TMIII=302.9

TMV=1090.

TMIIIV=1511.

DSIII=0.004411

DSV=0.0047

DSIIIV=0.01664

DCIII=-0.00005

DCV=0.001

AXS=4.666

BXS=-0.008741

GO TO 60

C

C IN-P SYSTEM

C

50 TMIII=429.8

TMV=313.3

TMIIIV=1332.2

DSIII=0.001815

```

DSV=0.0005011
DSIII=0.01081
DCIII=-0.0002
DCV=0.000472
AXS=32.75
BXS=-0.02895
60 CONTINUE
C
C BINARY ROOT FINDING ROUTINE FOR THE GROUP III AND V
CCOMPOSITIONS
C
  XV=0.5
  XMIN=0.0
  XMAX=1.0
  R=0.0019872
  THETA1=T
  XOLD=0.4
  THTOLD=THETA2(XOLD)
  DO 100 I=1,50
    THET2=THETA2(XV)
    ERR=(THET2-THETA1)/THETA1
    IF(ABS(ERR).LT.0.0001) GO TO 200
    SWTCH=(THET2-THTOLD)/(XV-XOLD)
    THTOLD=THET2
    XOLD=XV
    IF(SWTCH.GT.0.AND.THET2.LT.THETA1) GO TO 80
    IF(SWTCH.LT.0.AND.THET2.GT.THETA1) GO TO 80
    XMAX=XV
    XV=0.5*(XMIN+XV)
    GO TO 100
  80 XMIN=XV
    XV=0.5*(XMAX+XV)
  100 CONTINUE
    WRITE(IWRT,120)
  120 FORMAT('0','***** SUBROUTINE STEADY: ITERATION FOR SOURCE ',
    & 'COMPOSITION DID NOT CONVERGE')
  200 CONTINUE
C
C CALCULATE THE STANDARD CHEMICAL POTENTIAL OF THE SOURCE
CSOLUTION
C
  DGA=(1.0-XV)*(DSIII*(TMIII-T)+DCIII*(T-TMIII-T*ALOG(T/TMIII)))
  DGB=XV*(DSV*(TMV-T)+DCV*(T-TMV-T*ALOG(T/TMV)))

```

```

      DGC=(AXS+BXS*T)*XV*(1.-XV)+R*T*(XV*ALOG(XV)+(1.-XV)*ALOG(1.-
XV))

```

```

      STDCP(VSC)=DGA+DGB+DGC

```

```

C

```

```

C LOCATE THE GROUP III AND V ELEMENTS IN THE ELEMENTAL
CABUNDANCE ARRAY

```

```

C AND INSERT THE CALCULATED ABUNDANCES INTO THIS ARRAY

```

```

C

```

```

      IDX3=0

```

```

      IDX5=0

```

```

      DO 300 I=1,IDIM2

```

```

      IF(ISS.EQ.2) GO TO 250

```

```

      IF(ELMNT(I).EQ.GA) IDX3=I

```

```

      IF(ELMNT(I).EQ.AS) IDX5=I

```

```

      GO TO 300

```

```

250 IF(ELMNT(I).EQ.IN) IDX3=I

```

```

      IF(ELMNT(I).EQ.P) IDX5=I

```

```

300 CONTINUE

```

```

      A(VSC,IDX3)=1.0-XV

```

```

      A(VSC,IDX5)=XV

```

```

      XIII=1.0-XV

```

```

      RETURN

```

```

      END

```

```

      SUBROUTINE

```

```

TOTSI(A,ELMNT,FRAC,N,SITOT,SIMF,ACTSIS,T,P,IDIM1,IDIM2,
&      V,E)

```

```

C

```

```

C SUBROUTINE TO CALCULATE THE TOTAL SI IN THE VAPOR PHASE

```

```

C AND THE ACTIVITY OF SI IN A SOLID SOLUTION

```

```

C

```

```

      DIMENSION A(IDIM1,IDIM2)

```

```

      INTEGER ELMNT(IDIM2),V,E,SIVPR/SI/

```

```

      REAL*8 N(IDIM1),FRAC(IDIM1)

```

```

      T0=298.15

```

```

      P0=101325.0

```

```

      RT=0.0019872*T

```

```

C

```

```

C DETERMINE THE TOTAL AMOUNT OF SILICON IN THE VAPOR

```

```

C

```

```

      SITOT=0.0

```

```

      SIMF=0.0

```

```

      ACTSIS=0.

```

```

      DO 100 J=1,E

```

```

      KSI=J

```

```

      IF(ELMNT(J).EQ.SIVPR) GO TO 130
100 CONTINUE
      GO TO 300
130 CONTINUE
      DO 140 I=1,V
      IF(A(I,KSI).LT.0.001) GO TO 140
      SITOT=SITOT+N(I)
      SIMF=SIMF+FRAC(I)
140 CONTINUE
C
C FIND SI(V) AND CALCULATE THE ACTIVITY OF SOLID SI IN SOLUTION
C
      DO 200 I=1,V
      ICNT=0
      IF(A(I,KSI).LT.0.001) GO TO 200
      DO 150 J=1,E
      IF(A(I,J).LT.0.001) GO TO 150
      ICNT=ICNT+1
150 CONTINUE
      IF(ICNT.GT.1) GO TO 200
      DG=108.-0.00091*(T-T0)-5.011E-7/2.*(T**2-T0**2)-147.6*(1/T-1/T0)
      & -T*(0.035637-0.00091*ALOG(T/T0)-5.011E-7*(T-T0)
      & -147.6/2.*(1/T**2-1/T0**2))
      ACTSIS=FRAC(I)*P/P0*EXP(DG/RT)
      IF(N(I).LT.1.00E-38) ACTSIS=0.
      GO TO 300
200 CONTINUE
300 CONTINUE
      RETURN
      END
      SUBROUTINE RATIO(A,ELMNT,FRAC,N,STDCP,ACTGAS,ACTINS,ACTASS,
      & ACTPS,RIII,V,RGAAS,RINP,T,P,T0,P0,IDIM1,IDIM2,V,E)
C
C THIS SUBROUTINE CALCULATES THE VAPOR III/V RATIO,
C THE GA, IN, AS AND P SOLID SOLUTION ACTIVITIES,
C AND THE SATURATION RATIOS OF GA-AS AND IN-P.
C
      DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1),KIII(5),KV(5)
      REAL*8 N(IDIM1),FRAC(IDIM1)
      INTEGER ELMNT(IDIM2),ELIII(5),ELV(5),V,E
      DATA ELIII(1)/'B'/,ELIII(2)/'AL'/,ELIII(3)/'GA'/,ELIII(4)/'IN'/,
      & ELIII(5)/'TL'/,ELV(1)/'N'/,ELV(2)/'P'/,ELV(3)/'AS'/,
      & ELV(4)/'SB'/,ELV(5)/'BI'/
      FNCDG(T)=DH+A1*(T-T0)+A2/2.*(T**2-T0**2)-A3*(1/T-1/T0)

```

```

& +A4*(T*ALOG(T)-T-T0*ALOG(T0)+T0)+A5/3.*(T**3-T0**3)
& -T*(DS+A1*ALOG(T/T0)+A2*(T-T0)-A3/2.*(1/T**2-1/T0**2)
& +A4/2.*(ALOG(T)**2-ALOG(T0)**2)+A5/2.*(T**2-T0**2))
RT=0.0019872*T

```

C

C DETERMINE WHICH INDECIES CORRESPOND TO COLUMN III AND V
ELEMENTS

C

```

DO 100 K=1,5
KIII(K)=0
KV(K)=0
DO 100 J=1,E
IF(ELMNT(J).EQ.ELIII(K)) KIII(K)=J
IF(ELMNT(J).EQ.ELV(K)) KV(K)=J
100 CONTINUE

```

C

C SUM-UP THE GROUP III AND V SPECIES AND CALCULATE THE RATIO

C

```

SUMIII=0.0
SUMV=0.0
DO 200 I=1,V
DO 200 K=1,5
IDXIII=KIII(K)
IDXV=KV(K)
IF(IDXIII.EQ.0) GO TO 120
SUMIII=SUMIII+A(I,IDXIII)*FRAC(I)
120 CONTINUE
IF(IDXV.EQ.0) GO TO 200
SUMV=SUMV+A(I,IDXV)*FRAC(I)
200 CONTINUE
RIIIIV=1.0E10
IF(SUMV.GT.0.0) RIIIV=SUMIII/SUMV

```

C

C FIND THE SPECIES: GA(V), IN(V), P(V) AND AS(V)

C AND CALCULATE THE ACTIVITIES FOR GA, IN, AS AND P IN A SOLID
CSOLUTION

C

```

ACTGAS=0.
ACTINS=0.
ACTASS=0.
ACTPS=0.
KGA=0
KAS=0
KIN=0

```


KP=0

C

C GA DATA

C

KSPC=KIII(3)

A1=0.023738

A2=2.09E-6

A3=-266.2

A4=-0.003812

A5=0.

DH=65.0

DS=0.030617

DO 400 IJK=1,4

GO TO(245,220,230,240),IJK

C

C INDIUM DATA

C

220 KSPC=KIII(4)

A1=-0.001015

A2=-1.614E-6

A3=0.

A4=0.

A5=-1.689E-9

DH=57.3

DS=0.027687

GO TO 245

C

C PHOSPHOROUS (P) DATA

C

230 KSPC=KV(2)

A1=-0.000732

A2=0.

A3=0.

A4=0.

A5=0.

DH=75.62

DS=0.02916

GO TO 245

C

C ARSENIC (AS) DATA

C

240 KSPC=KV(3)

A1=-0.001768

A2=-1.5E-6

```

A3=15.04
A4=0.0001967
A5=0.
DH=68.7
DS=0.033081
245 IF(KSPC.EQ.0) GO TO 400
DO 300 I=1,V
ICNT=0
IF(A(I,KSPC).LT.0.001) GO TO 300
DO 250 J=1,E
IF(A(I,J).LT.0.001) GO TO 250
ICNT=ICNT+1
250 CONTINUE
IF(ICNT.GT.1) GO TO 300
IF(A(I,KSPC).GT.1.001) GO TO 300
DG=FNCDG(T)
ACTIV=FRAC(I)*P/P0*EXP(DG/RT)
IF(UK.EQ.1) ACTGAS=ACTIV
IF(UK.EQ.1) KGA=I
IF(UK.EQ.2) ACTINS=ACTIV
IF(UK.EQ.2) KIN=I
IF(UK.EQ.3) ACTPS=ACTIV
IF(UK.EQ.3) KP=I
IF(UK.EQ.4) ACTASS=ACTIV
IF(UK.EQ.4) KAS=I
GO TO 400
300 CONTINUE
400 CONTINUE
C
C CALCULATE THE SATURATION RATIOS FOR GA-AS AND IN-P.
C
RGAAS=0.
RINP=0.
C
C GA-AS SYSTEM SATURATION RATIO
C
A1=0.01046
A2=2.8E-6
A3=0.
A4=0.
A5=0.
DH=-19.52
DS=-0.002948
K3=KGA

```

```

K5=KAS
DO 500 I=1,2
IF(K3.EQ.0.OR.K5.EQ.0) GO TO 470
IF(N(K3).LT.1.00E-38.OR.N(K5).LT.1.00E-38) GO TO 470
DG=STDCP(K3)+STDCP(K5)-FNCDG(T)/RT
RSAT=FRAC(K3)*FRAC(K5)*P**2*EXP(DG)/P0**2
IF(I.EQ.1) RGAAS=RSAT
IF(I.EQ.2) RINP=RSAT
C
C IN-P SYSTEM SATURATION RATIO
C
470 A1=0.01227
A2=0.
A3=-114.0
DH=-14.0
DS=-0.00936
K3=KIN
K5=KP
500 CONTINUE
RETURN
END
SUBROUTINE
OPTBAS(N,BESTN,A,D,DPRME,STDCP,SPECIE,PHASE,A0,A1,A2,
&A3,BQUES,DH0,DS0,ICP,IDXBAS,ITER,IDIM1,IDIM2,V,S,C,E,ISTOP,ICHNG,
&IWRT,FRAC)
C
C THIS SUBROUTINE DETERMINES THE OPTIMUM SET OF BASIS SPECIES
C
  DIMENSION A(IDIM1,IDIM2),D(IDIM2,IDIM2),IDXBAS(IDIM2),
&    STDCP(IDIM1),A0(IDIM1),A1(IDIM1),A2(IDIM1),A3(IDIM1),
&    DH0(IDIM1),DS0(IDIM1),ICP(IDIM1)
  REAL*8 N(IDIM1),BESTN(IDIM1),DPRME(IDIM2,IDIM2),TEMP,FRAC(IDIM1)
  INTEGER SPECIE(IDIM1,3),PHASE(IDIM1,3),BQUES(IDIM1),V,S,C,E,VSC,
&    VSCM1
  ISTOP=0
  ICHNG=0
  VSC=V+S+C
  VSCM1=VSC-1
C
C BUBBLE SORT THE N VECTOR INTO DESCENDING ORDER
C AND ORDER STDCP, A, DH0, DS0, A0, A1, A2, A3, SPECIE, PHASE
C AND ICP CORRESPONDINGLY
C
  DO 300 I=1,VSCM1

```

```

IP1=I+1
DO 200 II=IP1,VSC
IF(N(II).LE.N(I)) GO TO 200
ICHNG=1
TEMP=N(I)
N(I)=N(II)
N(II)=TEMP
TEMP=BESTN(I)
BESTN(I)=BESTN(II)
BESTN(II)=TEMP
TEMP=FRAC(I)
FRAC(I)=FRAC(II)
FRAC(II)=TEMP
TEMP=STDCP(I)
STDCP(I)=STDCP(II)
STDCP(II)=TEMP
TEMP=A0(I)
A0(I)=A0(II)
A0(II)=TEMP
TEMP=A1(I)
A1(I)=A1(II)
A1(II)=TEMP
TEMP=A2(I)
A2(I)=A2(II)
A2(II)=TEMP
TEMP=A3(I)
A3(I)=A3(II)
A3(II)=TEMP
TEMP=DH0(I)
DH0(I)=DH0(II)
DH0(II)=TEMP
TEMP=DS0(I)
DS0(I)=DS0(II)
DS0(II)=TEMP
ITEMP=BQUES(I)
BQUES(I)=BQUES(II)
BQUES(II)=ITEMP
ITEMP=ICP(I)
ICP(I)=ICP(II)
ICP(II)=ITEMP
DO 50 J=1,3
ITEMP=SPECIE(I,J)
SPECIE(I,J)=SPECIE(II,J)
SPECIE(II,J)=ITEMP

```

```

      ITEMP=PHASE(I,J)
      PHASE(I,J)=PHASE(II,J)
      PHASE(II,J)=ITEMP
50  CONTINUE
      DO 100 J=1,E
      TEMP=A(I,J)
      A(I,J)=A(II,J)
      A(II,J)=TEMP
100  CONTINUE
200  CONTINUE
300  CONTINUE
C
C  IF THE PREVIOUSLY USED BASIS IS STILL THE OPTIMUM BASIS
C  SKIP THE REST OF THIS SUBROUTINE AND CONTINUE WITH THE
CCALCULATIONS
C
      IF(ITER.GT.1.AND.ICHNG.EQ.0) GO TO 480
C
C  BUILD THE D MATRIX WHICH WILL CONTAIN THE OPTIMUM BASIS
C
      DO 320 J=1,E
      DPRME(1,J)=A(1,J)
320  CONTINUE
      MA=0
      DO 400 MD=1,E
340  MA=MA+1
      IF(MA.GT.VSC) GO TO 450
      DO 350 J=1,E
      D(MD,J)=A(MA,J)
350  CONTINUE
      IDXBAS(MD)=MA
      IF(MD.EQ.1) GO TO 400
      CALL TESTD(D,DPRME,MD,E,IDIM2,ITST)
      IF(ITST.EQ.0) GO TO 340
400  CONTINUE
      GO TO 480
450  WRITE(IWRT,460) ITER
460  FORMAT('0','***** ITERATION ',I5,' AN OPTIMUM SET OF BASIS ',
      &'SPECIES COULD NOT BE FOUND FOR THIS SYSTEM IN SUBROUTINE
OPTBAS')
      ISTOP=1
480  RETURN
      END
      SUBROUTINE TESTD(D,DPRME,MD,E,IDIM2,ITST)

```

```

C
C THIS SUBROUTINE TESTS THE D MATRIX FOR LINEAR DEPENDENCE
C USING A GRAM-SCHMIDT ORTHOGONALIZATION ALGORITHM
C
  DIMENSION D(IDIM2,IDIM2)
  REAL*8 DPRME(IDIM2,IDIM2),ANUM,DENOM
  INTEGER E
  ITST=0
  DO 100 J=1,E
    DPRME(MD,J)=D(MD,J)
100 CONTINUE
  MDM1=MD-1
  DO 400 L=1,MDM1
    ANUM=0.0
    DENOM=0.0
    DO 200 K=1,E
      ANUM=ANUM+D(MD,K)*DPRME(L,K)
      DENOM=DENOM+DPRME(L,K)**2
200 CONTINUE
    DO 300 J=1,E
      DPRME(MD,J)=DPRME(MD,J)-DPRME(L,J)*ANUM/DENOM
300 CONTINUE
400 CONTINUE
C
C TEST FOR "ZEROS" ON THE NEW ROW
C
  DO 500 J=1,E
    IF(DABS(DPRME(MD,J)).GT.1.0D-5) ITST=ITST+1
500 CONTINUE
  RETURN
  END
  SUBROUTINE EQCON(A,D,DD,DINV,DG,GNU,STDCP,KEQ,IDXBAS,WKA,
&      IDIM1,IDIM2,V,S,C,E,ISTOP)
C
C THIS SUBROUTINE CALCULATES THE REACTION COEFFICIENT MATRIX
C AND THE EQUILIBRIUM CONSTANTS FOR THE FORMATION REACTIONS
C
  DIMENSION A(IDIM1,IDIM2),D(IDIM2,IDIM2),DD(IDIM2,IDIM2),
&      DINV(IDIM2,IDIM2),GNU(IDIM1,IDIM2),
&      IDXBAS(IDIM2),STDCP(IDIM1),WKA(IDIM2)
  DOUBLE PRECISION DD,DINV,WKA,DG(IDIM1),ARG
  INTEGER V,S,C,E,VSC
  REAL*8 KEQ(IDIM1)
  VSC=V+S+C

```

```

      ISTOP=0
C
C STORE ARRAY D IN ARRAY DD AND USE ARRAY DD IN THE CALL TO
CLINV1F
C
      DO 100 I=1,E
      DO 100 J=1,E
      DD(I,J)=D(I,J)
100 CONTINUE
C
C INVERT MATRIX DD USING IMSL SUBROUTINE LINV1F
C
      IDGT=4
      CALL LINV1F(DD,E,IDIM2,DINV,IDGT,WKA,IER)
      IF(IER.EQ.129) ISTOP=1
      IF(ISTOP.EQ.1) GO TO 600
C
C CALCULATE THE REACTION COEFFICIENT MATRIX
C
      DO 300 I=1,VSC
      DO 300 J=1,E
      TEMP=0.0
      DO 200 JJ=1,E
      TEMP=TEMP+A(I,JJ)*DINV(JJ,J)
200 CONTINUE
      GNU(I,J)=TEMP
300 CONTINUE
C
C CALCULATE THE EQUILIBRIUM CONSTANTS FOR THE FORMATION
CREACTIONS
C
      DO 500 I=1,VSC
      DO 501 J=1,E
      IF(LEQ.IDXBAS(J)) GO TO 500
501 CONTINUE
      ARG=(-1.0)*STDPC(I)
      DO 400 K=1,E
      IDXB=IDXBAS(K)
      ARG=ARG+GNU(I,K)*STDPC(IDXB)
400 CONTINUE
      DG(I)=ARG
      IF(ARG.GT.500.0) ARG=500.0
      KEQ(I)=DEXP(ARG)
500 CONTINUE

```

600 RETURN

END

SUBROUTINE ACTCOF(FRAC,ACOE,ISPCE,SPECIE,INDEX,IDIM1,RELMAX,
& IXSCOR,AXS,BXS,T,IACFF,V,S,C,IWRT,FS1)

C

C SUBROUTINE TO CALCULATE ACTIVITY COEFFICIENTS FOR THE
CSOLUTION PHASE

C

C IXSCOR ALGORITHM

C 1 BINARY SIMPLE SOLUTION THEORY $GE=(AXS+BXS*T)*X1*X2$

C 2 HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE

CH=AXS*EXP(BXS/T)

C 3 QUASI-CHEMICAL EQUILIBRIUM MODEL (STRINGFELLOW)

C 4 MODEL FOR LIQUID SOLUTION OF GA-IN

C 5 MODEL S.R.O.P. PLUS D.L.P.

C 6 TITANIUM CARBIDE MODEL

C

DIMENSION INDEX(IDIM1)

INTEGER ISPCE(IDIM1,3),SPECIE(IDIM1,3),V,S,C,VSC

REAL*8 FRAC(IDIM1),ACOE(IDIM1),X1,X2,DX,POLG,DPOLG,FS1

VSC=V+S+C

DO 100 I=1,VSC

ACOE(I)=1.0D+00

100 CONTINUE

C CHECK TO SEE IF WE NEED TO USE A SOLUTION MODEL YET

IF(ABS(RELMAX).LT.0.1) IACFF=1

IF(IXSCOR.EQ.2) IACFF=1

IF(IXSCOR.EQ.3) IACFF=1

IF(IXSCOR.EQ.4) IACFF=1

IF(IXSCOR.EQ.5) IACFF=1

IF(IXSCOR.EQ.6) IACFF=1

IF(IXSCOR.LT.1.OR.IXSCOR.GT.6.OR.S.LE.1) IACFF=0

IF(IACFF.EQ.0) GO TO 900

RT=0.0019872*T

C

C IDENTIFY THE SOLUTION SPECIES

C

DO 150 J=1,S

K=V+J

DO 150 I=1,VSC

IF(SPECIE(I,1).EQ.ISPCE(K,1).AND.

& SPECIE(I,2).EQ.ISPCE(K,2).AND.

& SPECIE(I,3).EQ.ISPCE(K,3)) INDEX(J)=I

150 CONTINUE


```

ITEST=1
DO 155 J=1,S
  IF(INDEX(J).LT.1.OR.INDEX(J).GT.VSC) ITEST=0
155 CONTINUE
  IF(ITEST.EQ.0) WRITE(IWRT,160)
160 FORMAT('0','***** THE SOLUTION SPECIES COULD NOT BE
&IDENTIFIED',
&      ' IN SUBROUTINE ACTCOF')
  IF(IXSCOR.EQ.2) GO TO 200
  IF(IXSCOR.EQ.3) GO TO 300
  IF(IXSCOR.EQ.4) GO TO 400
  IF(IXSCOR.EQ.5) GO TO 500
  IF(IXSCOR.EQ.6) GO TO 600
C
C BINARY SIMPLE SOLUTION THEORY
C
  IDX1=INDEX(1)
  IDX2=INDEX(2)
  X1=FRAC(IDX1)
  X2=1.0-X1
  ARG1=(AXS+BXS*T)*X2**2/RT
  ARG2=(AXS+BXS*T)*X1**2/RT
  ACOEF(IDX1)=DEXP(ARG1)
  ACOEF(IDX2)=DEXP(ARG2)
  GO TO 900
C
C HENRY'S CONSTANT FOR THE FIRST SOLUTION SPECIE
C
200 IDX1=INDEX(1)
  ACOEF(IDX1)=AXS*EXP(BXS/T)
  GO TO 900
C
C STRINGFELLOW'S QUASI-CHEMICAL EQUILIBRIUM MODEL
C
300 IDX1=INDEX(1)
  IDX2=INDEX(2)
C OMEGA IS ONE OF HIS PARAMETERS, DEPENDS ON BINARY PAIR
  OMEGA=AXS
C Z IS THE NUMBER OF NEAREST NEIGHBORS
  Z=BXS
  X1=FRAC(IDX1)
  X2=1.0-X1
  ETA=EXP(OMEGA/(Z*RT))
  BETA=(1.0+4.0*X1*X2*(ETA**2.0-1.0))*0.5

```

```

ACOEF(IX1)=((BETA-1.0+2.0*X1)/(X1*(BETA+1.0)))**(Z/2.0)
ACOEF(IX2)=((BETA+1.0-2.0*X1)/(X2*(BETA+1.0)))**(Z/2.0)
GO TO 900
C
C MODEL FOR LIQUID SOLUTION OF GA-IN
C
400 IX1=INDEX(1)
    IX2=INDEX(2)
    X1=FRAC(IX1)
    X2=1.0-X1
    AKOEF1=(X2**2./(RT*4.184E3))*(4450.+T*(1.19185+.25943*(3.-4.*X2)))
    AKOEF2=(X1**2./(RT*4.184E3))*(4450.+T*(1.19185+.25943*(3.-4.*X1)))
    ACOEF(IX1)=DEXP(AKOEF1)
    ACOEF(IX2)=DEXP(AKOEF2)
    GO TO 900
C
C MODEL S.R.O.P. PLUS D.L.P.
C
500 IX1=INDEX(1)
    IX2=INDEX(2)
C AXS IS THE D.L.P. COEFF
C Z IS THE NUMBER OF NEAREST NEIGHBORS
    Z=BXS
    X1=FRAC(IX1)
    X2=1.0-X1
    AF1=(AXS*X2**2/RT)*(1.0+(2.*(2.*X1-1.)*ALOG(X2)-X1*4.*ALOG(X1))/Z)
    AF2=(AXS*X1**2/RT)*(1.0+(2.*(1.-2.*X1)*ALOG(X1)-X2*4.*ALOG(X2))/Z)
    ACOEF(IX1)=DEXP(AF1)
    ACOEF(IX2)=DEXP(AF2)
    GO TO 900
C
C TITANIUM CARBIDE MODEL
C
600 IX1=INDEX(1)
    IX2=INDEX(2)
    X1=FS1
    X2=1.0D+00-X1
C-----
R=1.987
A0=-171340.0
B0=27.243
A1=-57886.0
B1=11.877
A2=499502.0

```

```

B2=-176.677
A3=450862.0
B3=-237.296
C0=A0+B0*T
C1=A1+B1*T
C2=A2+B2*T
C3=A3+B3*T
DX=2.0*X1-1.0D+00
POLG=C0+C1*DX+C2*DX**2+C3*DX**3
DPOLG=2.0*C1+4.0*C2*DX+6.0*C3*DX**2
C-----
  ACOEF(IDX1)=DEXP(((1.0-X1)**2)*(POLG+X1*DPOLG)/(R*T))
  ACOEF(IDX2)=DEXP((X1**2)*(POLG-(1.0D+00-X1)*DPOLG)/(R*T))
C-----
900 RETURN
  END
  SUBROUTINE
CALCQ(GNU,N,ACOE,FRAC,PHASE,VAPOR,SOLN,IDXBAS,Q,
&      ZV,FRACZ,P,P0,V,S,C,E,IDIM1,IDIM2)
C
C SUBROUTINE TO CALCULATE EQUILIBRIUM CONSTANTS FROM
COMPOSITION
C
  DIMENSION GNU(IDIM1,IDIM2),IDXBAS(IDIM2)
  INTEGER V,S,C,E,VSC,PHASE(IDIM1,3),VAPOR(3),SOLN(3)
  REAL*8 N(IDIM1),NV,NS,Q(IDIM1),FRAC(IDIM1),ACOEF(IDIM1)
  VSC=V+S+C
C
C CALCULATE THE TOTAL NUMBER OF MOLES IN EACH PHASE
C
  NS=0.0
  NV=ZV
  DO 100 I=1,VSC
    IF(PHASE(I,1).EQ.VAPOR(1)) NV=NV+N(I)
    IF(PHASE(I,1).EQ.SOLN(1)) NS=NS+N(I)
  100 CONTINUE
C
C CALCULATE THE MOLE FRACTIONS
C
  DO 200 I=1,VSC
    FRAC(I)=1.0
    IF(PHASE(I,1).EQ.VAPOR(1)) FRAC(I)=N(I)/NV
    IF(PHASE(I,1).EQ.SOLN(1)) FRAC(I)=N(I)/NS
  200 CONTINUE

```

```

      FRACZ=ZV/NV
C
C CALCULATE THE EQUILIBRIUM CONSTANTS
C
      DO 400 I=1,VSC
      DO 401 J=1,E
      IF(LEQ.IDXBAS(J)) GO TO 400
401 CONTINUE
      PP0=1.0
      IF(PHASE(I,1).EQ.VAPOR(1)) PP0=P/P0
      Q(I)=ACOE(I)*FRAC(I)*PP0
      DO 300 J=1,E
      K=IDXBAS(J)
      PP0=1.0
      IF(PHASE(K,1).EQ.VAPOR(1)) PP0=P/P0
      Q(I)=Q(I)/(ACOE(K)*FRAC(K)*PP0)**GNU(I,J)
300 CONTINUE
400 CONTINUE
      RETURN
      END
      SUBROUTINE
ADJEXT(N,Q,GNU,DZETA,IDXBAS,COND,PHASE,IDIM1,IDIM2,
&      V,S,C,E,DG,VAPOR,SOLN)
C
C SUBROUTINE TO ADJUST THE EXTENTS OF REACTION
C
      DIMENSION IDXBAS(IDIM2),GNU(IDIM1,IDIM2)
      INTEGER COND(3),PHASE(IDIM1,3),V,S,C,E,VSC,VAPOR(3),SOLN(3)

REAL*8N(IDIM1),DZETA(IDIM1),DENOM,TOTDN,Q(IDIM1),TEST,AKAPA,NTG,
&      NTSOL,DG(IDIM1)
      VSC=V+S+C
C
C CALCULATE THE CHANGE IN REACTION EXTENT FOR EACH REACTION
C
      NTG=0.0
      NTSOL=0.0
      DO 50 I=1,VSC
      IF(PHASE(I,1).EQ.VAPOR(1))NTG=NTG+N(I)
      IF(PHASE(I,1).EQ.SOLN(1))NTSOL=NTSOL+N(I)
50 CONTINUE
      DO 200 I=1,VSC
      DELI=1.0
      IF(PHASE(I,1).EQ.COND(1)) DELI=0.0

```

```

DENOM=DEL/N(I)
DZETA(I)=0.0
DO 100 J=1,E
K=IDXBAS(J)
IF(LEQ.K) GO TO 200
DELK=1.0
IF(PHASE(K,1).EQ.COND(1)) DELK=0.0
DENOM=DENOM+(DELK*GNU(I,J)**2)/N(K)
IF(PHASE(K,1).EQ.VAPOR(1)) DENOM=DENOM-(GNU(I,J)**2)/NTG
IF(PHASE(K,1).EQ.SOLN(1)) DENOM=DENOM-(GNU(I,J)**2)/NTSOL
100 CONTINUE
IF(DENOM.EQ.0.0) DENOM=1.0
DZETA(I)=(DG(I)-DLOG(Q(I)))/DABS(DENOM)
IF(DZETA(I).LT.0.0.AND.DABS(DZETA(I)).GT.N(I)
&      DZETA(I)=(-1.0)*N(I)
IF(N(I).LE.1.0D-50.AND.DZETA(I).LT.0.0) DZETA(I)=0.0
200 CONTINUE
C
C LIMIT THE MAXIMUM ALLOWABLE DZETA VALUES
C BASED ON NON-NEAGATIVITY OF THE BASIS SPECIES
C
AKAPA=1.0
DO 400 J=1,E
K=IDXBAS(J)
TOTDN=0.0
DO 300 I=1,VSC
TOTDN=TOTDN-GNU(I,J)*DZETA(I)
300 CONTINUE
TEST=N(K)+TOTDN*AKAPA
IF(TEST.LT.0.0.AND.N(K).GT.1.0D-50) AKAPA=(-1.0)*N(K)/TOTDN
400 CONTINUE
DO 500 I=1,VSC
DO 450 J=1,E
IF(LEQ.IDXBAS(J)) GO TO 500
450 CONTINUE
DZETA(I)=DZETA(I)*AKAPA
IF(N(I).LE.1.0D-15.AND.DZETA(I).LT.0.0.AND.PHASE(I,1).NE.COND(1))
&  DZETA(I)=N(I)*(DEXP(DG(I)-DLOG(Q(I)))-1.0D+00)
500 CONTINUE
RETURN
END
SUBROUTINE
CNVFR(N,NTMP,STDCP,ACOE,DZETA,GNU,IDXBAS,VAPOR,
&      SOLN,PHASE,ZV,RT,P,P0,RLXMIN,LAMBDA,IDIM1,

```

```

      &          IDIM2,V,S,C,E)
C
C SUBROUTINE TO CALCULATE THE CONVERGENCE FORCER LAMBDA
C
      DIMENSION IDXBAS(IDIM2),GNU(IDIM1,IDIM2),STDCP(IDIM1)
      INTEGER VAPOR(3),SOLN(3),PHASE(IDIM1,3),V,S,C,E,VSC
      REAL*8 N(IDIM1),NTEMP(IDIM1),DZETA(IDIM1),DGDLO,DGDL1,LAMBDA,
      &      RLXMIN,DGDLAM,ACOEFF(IDIM1)
      VSC=V+S+C
C
C CALCULATE DG/DLAMBDA AT LAMBDA=1.0
C
      LAMBDA=1.0D+00
      DO 100 I=1,VSC
      NTEMP(I)=N(I)
100 CONTINUE
      CALL
CORMOL(NTEMP,DZETA,GNU,IDXBAS,IDIM1,IDIM2,LAMBDA,VSC,E)

DGDLO=DGDLAM(N,NTEMP,STDCP,ACOEFF,PHASE,VAPOR,SOLN,ZV,RT,P,P0,
      &      IDIM1,VSC)
      IF(DGDLO.LT.0.0) GO TO 500
C
C CALCULATE DG/DLAMBDA AT LAMBDA=0.0
C
      DGDLO=(-1.0)*DGDLAM(NTEMP,N,STDCP,ACOEFF,PHASE,VAPOR,SOLN,ZV,
      &      RT,P,P0,IDIM1,VSC)
      IF(DGDLO.EQ.DGDL1) DGDLO=-DGDLO
      LAMBDA=DGDLO/(DGDLO-DGDL1)
      IF(LAMBDA.LE.0.0.OR.LAMBDA.GT.1.0) LAMBDA=RLXMIN
500 CONTINUE
      RETURN
      END
      FUNCTION
DGDLAM(N1,N2,STDCP,ACOEFF,PHASE,VAPOR,SOLN,ZV,RT,P,P0,
      &      IDIM1,VSC)
C
C SUBPROGRAM TO CALCULATE DG/DLAMBDA
C
      DIMENSION STDCP(IDIM1)
      INTEGER PHASE(IDIM1,3),VAPOR(3),SOLN(3),VSC
      REAL*8 N1(IDIM1),N2(IDIM1),NV,NS,ARG,DGDLO,DGDLAM,ACOEFF(IDIM1)
C

```

C CALCULATE THE TOTAL NUMBER OF MOLES IN THE SOLUTION AND
CVAPOR PHASES

C

```

NS=0.0
NV=ZV
DO 100 I=1,VSC
  IF(PHASE(I,1).EQ.VAPOR(1)) NV=NV+N2(I)
  IF(PHASE(I,1).EQ.SOLN(1)) NS=NS+N2(I)
100 CONTINUE

```

C

C CALCULATE DG/DLAMBDA

C

```

DGD L=0.0
DO 200 I=1,VSC
  ARG=1.0D+00
  IF(PHASE(I,1).EQ.VAPOR(1)) ARG=ACOE(I)*N2(I)*P/P0/NV
  IF(PHASE(I,1).EQ.SOLN(1)) ARG=ACOE(I)*N2(I)/NS
  DGD L=DGD L+(N2(I)-N1(I))*(STD C P(I)+DLOG(ARG))
200 CONTINUE
DGD LAM=DGD L*RT
RETURN
END
SUBROUTINE

```

CORMOL(N,DZETA,GNU,IDX BAS,IDIM1,IDIM2,LAMBDA,VSC,E)

C

C SUBROUTINE TO CORRECT THE MOLAR AMOUNTS OF EACH SPECIE

C

```

  DIMENSION GNU(IDIM1,IDIM2),IDX BAS(IDIM2)
  REAL*8 N(IDIM1),DZETA(IDIM1),LAMBDA
  INTEGER VSC,E

```

C

C CORRECT EACH NONBASIS SPECIE

C

```

  DO 200 I=1,VSC
    DO 100 J=1,E
      IF(I.EQ.IDX BAS(J)) GO TO 200
100 CONTINUE
    N(I)=N(I)+DZETA(I)*LAMBDA
    IF(N(I).LT.1.0D-50) N(I)=1.0D-50
200 CONTINUE

```

C

C CORRECT EACH BASIS SPECIE

C

```

  DO 400 J=1,E

```

```

      K=IDXBAS(J)
      DO 300 I=1,VSC
        N(K)=N(K)-GNU(I,J)*DZETA(I)*LAMBDA
300  CONTINUE
      IF(N(K).LT.1.0D-50) N(K)=1.0D-50
400  CONTINUE
      RETURN
      END
      SUBROUTINE ORDER(ISPCE,SPECIE,PHASE,N,A,STDCP,A0,A1,A2,A3,DH0,
&DS0,DZETA,CHMPT,ACOE,FRAC,QUES,DG,Q,KEQ,ICP,IDIM1,IDIM2,E,VSC)
C
C  SUBROUTINE TO ORDER THE ARRAYS BACK TO THE ORIGINAL ORDER
C  OF THE PROBLEM STATEMENT
C
      DIMENSION A(IDIM1,IDIM2),STDCP(IDIM1),A0(IDIM1),A1(IDIM1),
&A2(IDIM1),A3(IDIM1),DH0(IDIM1),DS0(IDIM1),ICP(IDIM1)
      INTEGER QUES(IDIM1),ISPCE(IDIM1,3),SPECIE(IDIM1,3),
&    PHASE(IDIM1,3),E,VSC,VSCM1
      REAL*8 N(IDIM1),DZETA(IDIM1),TEMP,Q(IDIM1),KEQ(IDIM1),DTEMP,
&FRAC(IDIM1),CHMPT(IDIM1),DG(IDIM1),ACOEF(IDIM1)
      VSCM1=VSC-1
      DO 300 I=1,VSCM1
        IP1=I+1
        DO 200 II=IP1,VSC
          IF(ISPCE(I,1).EQ.SPECIE(II,1).AND.
&  ISPCE(I,2).EQ.SPECIE(II,2).AND.
&  ISPCE(I,3).EQ.SPECIE(II,3)) GO TO 50
          GO TO 200
50  TEMP=N(I)
          N(I)=N(II)
          N(II)=TEMP
          TEMP=STDCP(I)
          STDCP(I)=STDCP(II)
          STDCP(II)=TEMP
          TEMP=A0(I)
          A0(I)=A0(II)
          A0(II)=TEMP
          TEMP=A1(I)
          A1(I)=A1(II)
          A1(II)=TEMP
          TEMP=A2(I)
          A2(I)=A2(II)
          A2(II)=TEMP
          TEMP=A3(I)

```



```

A3(I)=A3(II)
A3(II)=TEMP
TEMP=DH0(I)
DH0(I)=DH0(II)
DH0(II)=TEMP
TEMP=DS0(I)
DS0(I)=DS0(II)
DS0(II)=TEMP
ITEMP=ICP(I)
ICP(I)=ICP(II)
ICP(II)=ITEMP
DTEMP=DZETA(I)
DZETA(I)=DZETA(II)
DZETA(II)=DTEMP
TEMP=CHMPT(I)
CHMPT(I)=CHMPT(II)
CHMPT(II)=TEMP
DTEMP=ACOE(I)
ACOE(I)=ACOE(II)
ACOE(II)=DTEMP
DTEMP=FRAC(I)
FRAC(I)=FRAC(II)
FRAC(II)=DTEMP
ITEMP=QUES(I)
QUES(I)=QUES(II)
QUES(II)=ITEMP
DTEMP=DG(I)
DG(I)=DG(II)
DG(II)=DTEMP
TEMP=Q(I)
Q(I)=Q(II)
Q(II)=TEMP
DTEMP=KEQ(I)
KEQ(I)=KEQ(II)
KEQ(II)=DTEMP
DO 60 J=1,3
ITEMP=SPECIE(I,J)
SPECIE(I,J)=SPECIE(II,J)
SPECIE(II,J)=ITEMP
ITEMP=PHASE(I,J)
PHASE(I,J)=PHASE(II,J)
PHASE(II,J)=ITEMP
60 CONTINUE
DO 100 J=1,E

```

```

TEMP=A(I,J)
A(I,J)=A(II,J)
A(II,J)=TEMP
100 CONTINUE
200 CONTINUE
300 CONTINUE
RETURN
END
SUBROUTINE
WRAPUP(TITLE,SPECIE,INERT,N,FRAC,QUES,ZV,FRACZ,SITOT,
& SIMF,ACTSIS,ACTGAS,ACTINS,ACTPS,ACTASS,RHIV,RGAAS,RINP,
& BSTCVG,ITBST,RELMAX,CNVG,ISS,XIII,T,P,IDATA,IDIM1,IFILE,V,VSC,
& IOPT,ITP,NTP,ITAB,ICMP,IBL,ICOML,ICOMP1,ICOMP2)
C
C SUBROUTINE TO WRITE-OUT A SUMMARY OF THE RESULTS TO A FILE
C
  DIMENSION INERT(3),TEMP(20),PRESS(20),
& IDCOMP(55,3),CONV(55,20)
  INTEGER TITLE(20),SPECIE(IDIM1,3),QUES(IDIM1),V,VSC,
& EL(5)'SI','GA','IN','P','AS'
  REAL*8 N(IDIM1),FRAC(IDIM1),COMP(55,20),QUANT(55,20)
  IF(IDATA.EQ.0.AND.ICMP.EQ.1.AND.IBL.EQ.1)
& WRITE(ITAB,50) (TITLE(K),K=1,20)
  IF(IDATA.EQ.0.AND.ICMP.EQ.1.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,50) (TITLE(K),K=1,20)
  IF(IDATA.EQ.0.AND.IOPT.EQ.4) WRITE(ITAB,51) ICMP
  IF(IDATA.EQ.0.AND.ICOML.EQ.1) WRITE(ITAB,52) ICOMP1,ICOMP2
  IF(IDATA.EQ.0.AND.ICOML.GE.2) WRITE(ITAB,52) IBL,ICOMP2
  IF(IDATA.EQ.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,51) ICMP
50 FORMAT(/,1X,20A4)
51 FORMAT(/,/,1X,'COMPOSITIONAL SET # ',I3)
52 FORMAT(/,/,1X,'COMPOSITIONAL SET # ',I3,',',I3)
  IF(IOPT.EQ.1.OR.IOPT.EQ.4)TEMP(ITP)=T
  IF(IOPT.EQ.2.OR.IOPT.EQ.5)PRESS(ITP)=P/1.01325E+05
  IF(IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,55) T,P
55 FORMAT(1X,'TEMPERATURE = 'F7.1,' K',/, 'PRESSURE = 'E12.5,' PA')

IF(ABS(RELMAX).GT.CNVG.AND.IDATA.NE.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,58) RELMAX,CNVG,BSTCVG,ITBST
58 FORMAT(66('*'),/,*,5X,'ITERATION FOR EQUILIBRIUM COMPOSITION ',
& 'DID NOT CONVERGE',5X,*,/,*,1X,'MAXIMUM ERROR=',
& E12.5,2X,'CONVERGENCE CRITERION=',E12.5,1X,*,
&/,*,9X,'BEST CONVERGENCE=',E12.5,' AT ITERATION ',I4,8X,*,
&/,*,12X,'THE BEST OBTAINED RESULTS ARE SHOWN BELOW',11X,*,

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&    /,66('*'))
IF(IDATA.EQ.0) WRITE(ITAB,60)
IF(IDATA.EQ.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,60)
60 FORMAT(/,19X,'INITIAL COMPOSITIONS')
IF(IDATA.EQ.1.AND.IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,70)
70 FORMAT(13X,'EQUILIBRIUM COMPOSITIONS')
IF(IDATA.EQ.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,80)
IF(IDATA.EQ.0) WRITE(ITAB,80)
80 FORMAT(/,1X,'SPECIES',7X,'MOLE FRACTIONS',4X,'MOLE NUMBERS')
M=0
DO 200 I=1,VSC
  DO 201 L=1,3
    IDCOMP(I+M,L)=SPECIE(I,L)
201 CONTINUE
  COMP(I+M,ITP)=FRAC(I)
  QUANT(I+M,ITP)=N(I)
  IF(QUES(I).EQ.'?' )THEN
    CONV(I+M,ITP)='* '
    IA=1
  ELSE IF(QUES(I).EQ.'? ' )THEN
    CONV(I+M,ITP)='# '
    IB=1
  ELSE
    CONV(I+M,ITP)=' '
 ENDIF
  IF(IOPT.EQ.0.OR.IOPT.EQ.3)
    &    WRITE(IFILE,100) (SPECIE(I,K),K=1,3),FRAC(I),N(I),QUES(I)
  IF(I.NE.V) GO TO 200
  DO 202 J=1,3
    IDCOMP(V+1,J)=INERT(J)
202 CONTINUE
  COMP(V+1,ITP)=FRACZ
  QUANT(V+1,ITP)=ZV
  CONV(V+1,ITP)=' '
  M=1
  IF(IOPT.EQ.0.OR.IOPT.EQ.3)
    &    WRITE(IFILE,100) (INERT(K),K=1,3),FRACZ,ZV
100 FORMAT(3A4,2X,E12.5,2X,E12.5,1X,A4)
  IF(RIIIV.GT.0.AND.RIIIV.LT.1.0E6.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
    &    WRITE(IFILE,105) RIIIV
105 FORMAT('VAPOR III/V ',10X,F9.4)
  IF(SITOT.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
    &    WRITE(IFILE,110) SIMF,SITOT
110 FORMAT('SI IN VAPOR ',2X,E12.5,2X,E12.5)

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IF(ACTSIS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,120) EL(1),ACTSIS
120 FORMAT(1A2,' ACTIVITY',13X,E12.5)
IF(ACTGAS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,120) EL(2),ACTGAS
IF(ACTINS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,120) EL(3),ACTINS
IF(ACTPS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,120) EL(4),ACTPS
IF(ACTASS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3)
& WRITE(IFILE,120) EL(5),ACTASS
IF(RGAAS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,130) RGAAS
130 FORMAT('GA-AS SATURATION RATIO 'E12.5)
IF(RINP.GT.0) WRITE(IFILE,135) RINP
135 FORMAT(' IN-P SATURATION RATIO 'E12.5)
200 CONTINUE
IF(IDATA.EQ.0) WRITE(ITAB,101) ((IDCOMP(J,K),K=1,3),COMP(J,1),
&QUANT(J,1),J=1,VSC+1)
101 FORMAT(3A4,2X,E12.5,6X,E12.5)
IF(ISS.GT.0.AND.IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,205) XIII
205 FORMAT(3X,'X=',F6.4)
IF(IOPT.EQ.0.OR.IOPT.EQ.3) WRITE(IFILE,210)
210 FORMAT(' ')
IF(ITP.EQ.NTP.AND.IDATA.EQ.1)THEN
IF(IOPT.EQ.1.OR.IOPT.EQ.4)WRITE(ITAB,290) P/1.01325E+05
IF(IOPT.EQ.2.OR.IOPT.EQ.5)WRITE(ITAB,295) T
290 FORMAT(/,/, ' EQUILIBRIUM PRESSURE = 'F6.3, ' ATM')
295 FORMAT(/,/, ' EQUILIBRIUM TEMPERATURE = 'F7.1, ' K')
IF(IA.EQ.1.OR.IB.EQ.1)WRITE(ITAB,300)
300 FORMAT(/,72('$'),/,21X,'<<<< CONVERGENCE WARNING >>>>',/,
&72('$'))
IF(IB.EQ.1)WRITE(ITAB,301)
301 FORMAT(/, -- EQUILIBRIUM COMPOSITIONS PRECEDED BY THE
&SYMBOL ',
&('#) DID NOT CONVERGE.'/,4X,'THE DISCREPANCY IS LESS THAN 10% ',
&'OF DESIRED VALUE.'/,72('$'))
IF(IA.EQ.1)WRITE(ITAB,302)
302 FORMAT(/, -- EQUILIBRIUM COMPOSITIONS PRECEDED BY THE
&SYMBOL ',
&('* ) DID NOT CONVERGE.'/,4X,'THE DISCREPANCY IS MORE THAN 10% ',
&'OF DESIRED VALUE.'/,72('$'))
DO 235 ILOOP=1,2
IF(ILOOP.EQ.1)WRITE(ITAB,220)
IF(ILOOP.EQ.2)WRITE(ITAB,225)

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```

220 FORMAT(/,25X,'EQUILIBRIUM MOLE FRACTIONS')
225 FORMAT(/,/,26X,'EQUILIBRIUM MOLE NUMBERS')
  L=0
  M=0
270 L=M+1
  M=M+5
  IC=VSC+1-M
  IF(IC.GE.-4 .AND. IC.LE.0)THEN
    M=VSC+1
    GO TO 230
  ELSE IF(IC.GT.0)THEN
    GO TO 230
  ELSE
    GO TO 235
  END IF
230  IF(IOPT.EQ.1.OR.IOPT.EQ.4)THEN
    WRITE(ITAB,240) ((IDCOMP(I,J),J=1,3),I=L,M)
240  FORMAT(/,' TEMP(K)',1X,3(3A4,1X),2(3A4))
    DO 245 K=1,NTP
      IF(LOOP.EQ.1)WRITE(ITAB,250) TEMP(K),(CONV(J,K),COMP(J,K),
        &  J=L,M)
      IF(LOOP.EQ.2)WRITE(ITAB,250) TEMP(K),(CONV(J,K),QUANT(J,K),
        &  J=L,M)
250  FORMAT(F7.1,5(1X,A1,E11.5))
245  CONTINUE
    GO TO 270
  ELSE IF(IOPT.EQ.2.OR.IOPT.EQ.5)THEN
    WRITE(ITAB,255) ((IDCOMP(I,J),J=1,3),I=L,M)
255  FORMAT(/,' PRESS(ATM)',1X,15A4)
    DO 260 K=1,NTP
      IF(LOOP.EQ.1)WRITE(ITAB,265) PRESS(K),(COMP(J,K),CONV(J,K),
        &  J=L,M)
      IF(LOOP.EQ.2)WRITE(ITAB,265) PRESS(K),(QUANT(J,K),CONV(J,K),
        &  J=L,M)
265  FORMAT(F6.3,1X,5(1X,A1,E11.5))
260  CONTINUE
    GO TO 270
  ELSE
    GO TO 235
  END IF
235 CONTINUE
  ELSE
    IDATA=1
    GO TO 285

```

```

      END IF
285 RETURN
      END
      SUBROUTINE
GIBBS(N,STDCP,STDCPZ,ACOE,FRAC,ZV,FRACZ,COND,SOLN,
&      PHASE,RT,P,P0,IDIM1,V,S,C,GFE)
C
C SUBROUTINE TO CALCULATE THE GIBBS FREE ENERGY OF THE SYSTEM
C
      DIMENSION STDCP(IDIM1)
      REAL*8 N(IDIM1),FRAC(IDIM1),ARG,ACOE(IDIM1),GSTAR,GFE
      INTEGER COND(3),SOLN(3),PHASE(IDIM1,3),V,S,C,VSC
      VSC=V+S+C
C
C GAS CONSTANT IS IN UNITS OF: KCAL/G-MOLE-K
C
      ARG=1.0D+00
      IF(FRACZ.GT.0.0) ARG=FRACZ*P/P0
      GSTAR=ZV*(STDCPZ+ALOG(ARG))
      DO 150 I=1,VSC
      ARG=ACOE(I)*FRAC(I)*P/P0
      IF(PHASE(I,1).EQ.COND(1)) ARG=1.0D+00
      IF(PHASE(I,1).EQ.SOLN(1)) ARG=ACOE(I)*FRAC(I)
      GSTAR=GSTAR+N(I)*(STDCP(I)+DLOG(ARG))
150 CONTINUE
      GFE=GSTAR*RT
      RETURN
      END
      SUBROUTINE DEBUG(N,DZETA,VSC,IDIM1,ITER,ALMBDA,GFE,
&      RMX,IWRT)
C
C ROUTINE TO WRITE-OUT N, DZETA, ALMBDA DURING THE ITERATION
CPROCESS
C
      REAL*8 N(IDIM1),DZETA(IDIM1),ALMBDA,GFE
      INTEGER VSC
      WRITE(IWRT,10) ITER,ALMBDA,GFE,RMX
10 FORMAT('0',ITERATION = 'I5,5X','LAMBDA = 'E14.7,
&      5X,'GIBBS FREE ENERGY = 'E14.7,' KCAL',
&      5X,'RELATIVE ERROR = 'E12.5/,1X,
&      'N-VALUES',T20,'DELTA-ZETA VALUES')
      DO 50 I=1,VSC
      WRITE(IWRT,20) N(I),DZETA(I)
20 FORMAT(1X,E14.7,T20,E14.7)

```

```

50 CONTINUE
  RETURN
  END
  SUBROUTINE PMAT(MATRIX,NDIM1,NDIM2,L1,L2,NAME,IWRT)
C
C SUBROUTINE TO WRITE-OUT REAL MATRICIES
C
  INTEGER*2 NAME(3)
  REAL MATRIX(NDIM1,NDIM2)
  WRITE(IWRT,10) (NAME(J),J=1,3)
10 FORMAT('0','MATRIX ',3A2)
  DO 100 I=1,L1
    WRITE(IWRT,20) (MATRIX(I,J),J=1,L2)
20 FORMAT(1X,10(E11.4,2X))
100 CONTINUE
  RETURN
  END
  SUBROUTINE DPMAT(DMTRIX,NDIM1,NDIM2,L1,L2,NAME,IWRT)
C
C SUBROUTINE TO WRITE-OUT DOUBLE PRECISION REAL MATRICIES
C
  DOUBLE PRECISION DMTRIX(NDIM1,NDIM2)
  INTEGER*2 NAME(3)
  WRITE(IWRT,10) (NAME(J),J=1,3)
10 FORMAT('0','MATRIX ',3A2)
  DO 100 I=1,L1
    WRITE(IWRT,20) (DMTRIX(I,J),J=1,L2)
20 FORMAT(1X,10(D11.4,2X))
100 CONTINUE
  RETURN
  END
  SUBROUTINE PVEC(VECTOR,NDIM,L,NAME,IWRT)
C
C SUBROUTINE TO WRITE-OUT REAL VECTORS
C
  INTEGER*2 NAME(3)
  REAL*8 VECTOR(NDIM)
  WRITE(IWRT,10) (NAME(J),J=1,3)
10 FORMAT('0','THE TRANSPOSED ',3A2,' VECTOR IS:')
  WRITE(IWRT,20) (VECTOR(J),J=1,L)
20 FORMAT(1X,10(E11.4,2X))
  RETURN
  END
  SUBROUTINE IPVEC(IVCTOR,NDIM,L,NAME,IWRT)

```

C

C SUBROUTINE TO WRITE-OUT INTEGER VECTORS

C

```

    DIMENSION IVCTOR(NDIM)
    INTEGER*2 NAME(3)
    WRITE(IWRT,10) (NAME(J),J=1,3)
10 FORMAT('0','THE TRANSPOSED ',3A2,' VECTOR IS:')
    WRITE(IWRT,20) (IVCTOR(J),J=1,L)
20 FORMAT(1X,10(1I1,2X))
    RETURN
    END
    SUBROUTINE LINVIF (A,N,IA,AINV,IDGT,WKAREA,IER)

```

C

C IMSL SUBROUTINE FOR INVERTING REAL MATRICIES

C

```

    DOUBLE PRECISION A(IA,N),AINV(IA,N),WKAREA(1),ZERO,ONE
    DATA      ZERO/0.0D0/,ONE/1.0D0/
    IER=0
    DO 10 I=1,N
    DO 5 J=1,N
    AINV(I,J) = ZERO
5  CONTINUE
    AINV(I,I) = ONE
10 CONTINUE
    CALL LEQTIFF (A,N,N,IA,AINV,IDGT,WKAREA,IER)
    IF (IER .EQ. 0) GO TO 9005
9000 CONTINUE
9005 RETURN
    END
    SUBROUTINE LEQTIFF (A,M,N,IA,B,IDGT,WKAREA,IER)

```

C

C IMSL SUBROUTINE LEQTIFF FOR SOLVING THE MATRIX PROBLEM $A \cdot X = B$

C

```

    DIMENSION      A(IA,1),B(IA,1),WKAREA(1)
    DOUBLE PRECISION  A,B,WKAREA,D1,D2,WA
    C      INITIALIZE IER
    C      FIRST EXECUTABLE STATEMENT
    IER=0
    C      DECOMPOSE A
    CALL LUDATF (A,A,N,IA,IDGT,D1,D2,WKAREA,WKAREA,WA,IER)
    IF (IER .GT. 128) GO TO 9005
    C      CALL ROUTINE LUELMF (FORWARD AND
    C      BACKWARD SUBSTITUTIONS)
    DO 10 J=1,M

```



```

      CALL LUELMF (A,B(1,J),WKAREA,N,IA,B(1,J))
10  CONTINUE
9005 RETURN
      END
      SUBROUTINE LUDATF (A,LU,N,IA,IDGT,D1,D2,IPVT,EQUIL,WA,IER)
C
C THIS SUBROUTINE IS USED WITH SUBROUTINE LEQT1F
C
      DIMENSION      A(IA,1),LU(IA,1),IPVT(1),EQUIL(1)
      DOUBLE PRECISION
A,LU,D1,D2,EQUIL,WA,ZERO,ONE,FOUR,SIXTN,SIXTH,
*      RN,WREL,BIGA,BIG,P,SUM,AI,WI,T,TEST,Q,IPVT
      DATA          ZERO,ONE,FOUR,SIXTN,SIXTH/0.D0,1.D0,4.D0,
*      16.D0,.0625D0/
C FIRST EXECUTABLE STATEMENT
C INITIALIZATION
IER = 0
RN = N
WREL = ZERO
D1 = ONE
D2 = ZERO
BIGA = ZERO
DO 10 I=1,N
  BIG = ZERO
  DO 5 J=1,N
    P = A(I,J)
    LU(I,J) = P
    P = DABS(P)
    IF (P .GT. BIG) BIG = P
5  CONTINUE
  IF (BIG .GT. BIGA) BIGA = BIG
  IF (BIG .EQ. ZERO) GO TO 110
  EQUIL(I) = ONE/BIG
10 CONTINUE
DO 105 J=1,N
  JM1 = J-1
  IF (JM1 .LT. 1) GO TO 40
C COMPUTE U(I,J), I=1,...,J-1
DO 35 I=1,JM1
  SUM = LU(I,J)
  IM1 = I-1
  IF (IDGT .EQ. 0) GO TO 25
C WITH ACCURACY TEST
  AI = DABS(SUM)

```

```

WI = ZERO
IF (IM1 .LT. 1) GO TO 20
DO 15 K=1,IM1
  T = LU(I,K)*LU(K,J)
  SUM = SUM-T
  WI = WI+DABS(T)
15  CONTINUE
  LU(I,J) = SUM
20  WI = WI+DABS(SUM)
  IF (AI .EQ. ZERO) AI = BIGA
  TEST = WI/AI
  IF (TEST .GT. WREL) WREL = TEST
  GO TO 35
C    WITHOUT ACCURACY
25  IF (IM1 .LT. 1) GO TO 35
  DO 30 K=1,IM1
    SUM = SUM-LU(I,K)*LU(K,J)
30  CONTINUE
    LU(I,J) = SUM
35  CONTINUE
40  P = ZERO
C    COMPUTE U(J,J) AND L(I,J), I=J+1,...,
DO 70 I=J,N
  SUM = LU(I,J)
  IF (IDGT .EQ. 0) GO TO 55
C    WITH ACCURACY TEST
  AI = DABS(SUM)
  WI = ZERO
  IF (JM1 .LT. 1) GO TO 50
  DO 45 K=1,JM1
    T = LU(I,K)*LU(K,J)
    SUM = SUM-T
    WI = WI+DABS(T)
45  CONTINUE
    LU(I,J) = SUM
50  WI = WI+DABS(SUM)
  IF (AI .EQ. ZERO) AI = BIGA
  TEST = WI/AI
  IF (TEST .GT. WREL) WREL = TEST
  GO TO 65
C    WITHOUT ACCURACY TEST
55  IF (JM1 .LT. 1) GO TO 65
  DO 60 K=1,JM1
    SUM = SUM-LU(I,K)*LU(K,J)

```

```

60  CONTINUE
    LU(I,J) = SUM
65  Q = EQUIL(I)*DABS(SUM)
    IF (P .GE. Q) GO TO 70
    P = Q
    IMAX = I
70  CONTINUE
C   TEST FOR ALGORITHMIC SINGULARITY
    IF (RN+P .EQ. RN) GO TO 110
    IF (J .EQ. IMAX) GO TO 80
C   INTERCHANGE ROWS J AND IMAX
    D1 = -D1
    DO 75 K=1,N
        P = LU(IMAX,K)
        LU(IMAX,K) = LU(J,K)
        LU(J,K) = P
75  CONTINUE
    EQUIL(IMAX) = EQUIL(J)
80  IPVT(J) = IMAX
    D1 = D1*LU(J,J)
85  IF (DABS(D1) .LE. ONE) GO TO 90
    D1 = D1*SIXTH
    D2 = D2+FOUR
    GO TO 85
90  IF (DABS(D1) .GE. SIXTH) GO TO 95
    D1 = D1*SIXTN
    D2 = D2-FOUR
    GO TO 90
95  CONTINUE
    JP1 = J+1
    IF (JP1 .GT. N) GO TO 105
C   DIVIDE BY PIVOT ELEMENT U(J,J)
    P = LU(J,J)
    DO 100 I=JP1,N
        LU(I,J) = LU(I,J)/P
100 CONTINUE
105 CONTINUE
C   PERFORM ACCURACY TEST
    IF (IDGT .EQ. 0) GO TO 9005
    P = 3*N+3
    WA = P*WREL
    IF (WA+10.D0*(-IDGT) .NE. WA) GO TO 9005
    IER = 34
    GO TO 9005

```

C ALGORITHMIC SINGULARITY

110 IER = 129

D1 = ZERO

D2 = ZERO

9005 RETURN

END

SUBROUTINE LUELMF (A,B,IPVT,N,IA,X)

C

C THIS SUBROUTINE IS USED WITH SUBROUTINE LEQT1F

C

DIMENSION A(IA,1),B(1),IPVT(1),X(1)

DOUBLE PRECISION A,B,X,SUM,IPVT

C FIRST EXECUTABLE STATEMENT

C SOLVE LY = B FOR Y

DO 5 I=1,N

5 X(I) = B(I)

IW = 0

DO 20 I=1,N

IP = IPVT(I)

SUM = X(IP)

X(IP) = X(I)

IF (IW .EQ. 0) GO TO 15

IM1 = I-1

DO 10 J=IW,IM1

SUM = SUM-A(I,J)*X(J)

10 CONTINUE

GO TO 20

15 IF (SUM .NE. 0.D0) IW = I

20 X(I) = SUM

C SOLVE UX = Y FOR X

DO 30 IB=1,N

I = N+1-IB

IP1 = I+1

SUM = X(I)

IF (IP1 .GT. N) GO TO 30

DO 25 J=IP1,N

SUM = SUM-A(I,J)*X(J)

25 CONTINUE

30 X(I) = SUM/A(I,I)

RETURN

END

SUBROUTINE SPECIL(N,A,E,V,S,SPECIE,ELMNT,IFILE)

C

C SUBROUTINE TO CALCULATE SPECIAL RATIOS FOR SPECIFIC SPECIES

C AT EQUILIBRIUM

C

```

REAL CLOUT, GAOUT, GEOUT, HOUT, INOUT, POUT, SIOUT, CLRAT,
&MGAOUT, MINOUT
REAL*8 N(50)
DIMENSION A(50,13)
INTEGER E, V, S, SPECIE(50,3), ELMNT(13), GA/GA', GE/GE', IN/IN',
&SA/AS', SI/SI', P/P', MAS/AS ('/, MGA/ GA-', MIN/ IN-',
&CL/CL'/, H/H'
ASOUT=0.0
CLOUT=0.0
GAOUT=0.0
GEOUT=0.0
HOUT=0.0
INOUT=0.0
POUT=0.0
SIOUT=0.0
MGAOUT=0.0
MINOUT=0.0
KAS=0.0
KCL=0.0
KGA=0.0
KGE=0.0
KH=0.0
KIN=0.0
KP=0.0
KSI=0.0
KMGA=0.0
KMIN=0.0

```

C

C CALCULATE THE TOTAL MOLES OF ELEMENTS IN THE VAPOR AT
CEQUILIBRIUM

C

```

DO 10, J=1,E
IF(ELMNT(J).EQ.SA) KAS=J
IF(ELMNT(J).EQ.CL) KCL=J
IF(ELMNT(J).EQ.GA) KGA=J
IF(ELMNT(J).EQ.GE) KGE=J
IF(ELMNT(J).EQ.H) KH=J
IF(ELMNT(J).EQ.IN) KIN=J
IF(ELMNT(J).EQ.P) KP=J
IF(ELMNT(J).EQ.SI) KSI=J

```

10 CONTINUE

C

```

C
DO 20, I=1,V
ASOUT=ASOUT+N(I)*A(I,KAS)
CLOUT=CLOUT+N(I)*A(I,KCL)
GAOUT=GAOUT+N(I)*A(I,KGA)
GEOUT=GEOUT+N(I)*A(I,KGE)
HOUT=HOUT+N(I)*A(I,KH)
INOUT=INOUT+N(I)*A(I,KIN)
POUT=POUT+N(I)*A(I,KP)
SIOUT=SIOUT+N(I)*A(I,KS)
20 CONTINUE
C
C CALCULATE CL/H RATIO IN THE VAPOR AT EQUILIBRIUM
C
IF(CLOUT .EQ. 0 .OR. HOUT .EQ. 0) GO TO 30
CLRAT=CLOUT/HOUT
WRITE(IFILE,205) CLRAT
205 FORMAT(1X,'CL/H =' ,E12.5)
WRITE(IFILE,200)
200 FORMAT(' ')
C
C CALCULATE GA/(GA+IN) RATIO IN THE VAPOR AT EQUILIBRIUM
C
30 IF(GAOUT .EQ. 0 .OR. INOUT .EQ. 0) GO TO 40
GARAT=GAOUT/(GAOUT+INOUT)
WRITE(IFILE,210) GARAT
210 FORMAT(1X,'GA/(GA+IN) (IN THE VAPOR) =' ,E12.5)
WRITE(IFILE,200)
C
C CALCULATE METAL CHLORINE RATION AT EQUILIBRIUM IN THE VAPOR
C
40 IF(CLOUT .EQ. 0) GO TO 60
IF(GEOUT .EQ. 0) GO TO 50
GERAT=GEOUT/CLOUT
WRITE(IFILE,220) GERAT
220 FORMAT(1X,'GE/CL =' ,E12.5)
50 IF(SIOUT .EQ. 0) GO TO 60
SIRAT=SIOUT/CLOUT
WRITE(IFILE,230) SIRAT
230 FORMAT(1X,'SI/CL =' ,E12.5)
IF(GEOUT .EQ. 0) GO TO 60
GSRAT=GEOUT/(GEOUT+SIOUT)
WRITE(IFILE,240)
240 FORMAT(1X,'GE/(GE+SI) =' ,E12.5)

```

```

C
C CALCULATE GA/(GA+IN) IN SOLUTION IN THE SOLID PHASE AT
CEQUILIBRIUM
C
60  IF(S.EQ. 0) GO TO 100
    DO 70, I=V+1,V+S
      IF(SPECIE(I,1).EQ.MGA.AND.SPECIE(I,2).EQ.MAS) KMGA=I
      IF(SPECIE(I,1).EQ.MIN.AND.SPECIE(I,2).EQ.MAS) KMIN=I
70  CONTINUE
    IF(KMGA.EQ.0 .OR. KMIN.EQ.0) GO TO 100
    MGAOUT=N(KMGA)
    MINOUT=N(KMIN)
    X=MGAOUT/(MGAOUT+MINOUT)
    WRITE(IFILE,250) X
250  FORMAT(1X,'X=GA-AS/(GA-AS+IN-AS) (IN SOLUTION) =' ,E12.5)
100  WRITE(IFILE,200)
    RETURN
    END

```

APPENDIX 2

FORTRAN ROUTINE FOR THE CALCULATION OF DEPOSITION PROFILES RESULTING IN A SINGLE CYLINDRICAL PORE MODEL OF CVI

c Program GNMX3.for: this program computes deposition profiles inside a cylindrical
c pore using the short distance asymptotic solution to the mass transfer Graetz-Nusselt
c problem.

c

```

    Dimension z(51),zl(51),d(51),Ts(51),k(51),Dfch4(51),Dfticl4(51),
    &    Dfhcl(51),Dkch4(51),Dkticl4(51),Dkhcl(51),Dch4(51),
    &    Dticl4(51),Dhcl(51),C(51),U(51),Alpch4(51),Alpticl4(51),
    &    Alphcl(51),T0ch4(51),T0ticl4(51),T0hcl(51),Resrch4(51),
    &    Resmch4(51),Xhcleq(51),Rx(51),Rd(51),Rrd(51,50),
    &    Xch4(51,7),Xticl4(51,7),Xhcl(51,7),dm(51)
    Real L,n,Mw,k,Nr,Nz
    Open(unit=1,file='gmassin.dat',status='old')
    Open(unit=2,file='gmassp3.dat',status='new')
    Open(unit=3,file='gmassx3.dat',status='new')
    Open(unit=4,file='gmasrd3.dat',status='new')
    Read(1,9) Dummy
    Read(1,10) Ft
    Read(1,10) P
    Read(1,10) Ts1
    Read(1,10) Ts2
    Read(1,10) Dp
    Read(1,10) L
    Read(1,10) n
    Read(1,10) Xoch4
    Read(1,10) Xoticl4
    Read(1,10) Xohcl
    Read(1,10) Mw
    Read(1,10) Den
    Read(1,10) Nz
    Read(1,10) Nr
    Read(1,10) tdis
    Read(1,10) tsto
    Read(1,10) tf
    9 format(f10.4,/,/)
    10 format(48x,f10.4)

```



```

Nt=tf/tdis
Ns=tf/tsto
do 20 i=1,Nz+1
d(i)=Dp
dm(i)=Dp
Rd(i)=0.0
do 30 j=1,Ns
Rrd(i,j)=0.0
30 continue
20 continue
it=1
ij=1
Xech4=Xoch4
Xeticl4=Xoticl4
Xehcl=Xohcl

c
c--- Beginning of time iteration loop -----
c
do 100 j=1,Nt
t=j*tdis
c
c--- Beginning of z-dir iteration loop -----
c
do 200 i=1,Nz+1
z(i)=(L/Nz)*(i-1)
zl(i)=z(i)/L
Ts(i)=((Ts2-Ts1)/L)*(z(i))+Ts1
k(i)=(0.08394)*exp(-5000.0/(Ts(i)+273.15))
Dfch4(i)=((3.89e-6)/P)*(ts(i)+273.15)**1.5
Dfticl4(i)=((7.5035e-6)/p)*(ts(i)+273.15)**1.5
Dfhcl(i)=((7.5035e-6)/p)*(ts(i)+273.15)**1.5
Dkch4(i)=(12.1253e-6)*d(i)*(ts(i)+273.15)**0.5
Dkticl4(i)=(8.028e-6)*d(i)*(ts(i)+273.15)**0.5
Dkhcl(i)=(8.028e-6)*d(i)*(ts(i)+273.15)**0.5
Dch4(i)=(Dfch4(i)*Dkch4(i))/(Dfch4(i)+Dkch4(i))
Dticl4(i)=(Dfticl4(i)*Dkticl4(i))/(Dfticl4(i)+Dkticl4(i))
Dhcl(i)=(Dfhcl(i)*Dkhcl(i))/(Dfhcl(i)+Dkhcl(i))
C(i)=(16.0345)*p/(Ts(i)+273.15)
U(i)=(54119.8)*(Ts(i)+273.15)*Ft/(n*P*d(i)**2.0)
Alpch4(i)=(8.0*Dch4(i)*(L/100.0))/(3.0*U(i)*(d(i)*(1e-6))**2)
Alpticl4(i)=(8.0*Dticl4(i)*(L/100.0))/(3.0*U(i)*(d(i)*(1e-6))**2)
Alphcl(i)=(8.0*Dhcl(i)*(L/100.0))/(3.0*U(i)*(d(i)*(1e-6))**2)
T0ch4(i)=(2.6789385/3.0)*(alpch4(i)**(1.0/3.0))
T0ticl4(i)=(2.6789385/3.0)*(alpticl4(i)**(1.0/3.0))
T0hcl(i)=(2.6789385/3.0)*(alphcl(i)**(1.0/3.0))

```

c

c--- Equilibrium Constant Calculation -----

c

if(j.eq.1) go to 201

Xech4=Xch4(i,1)

Xeticl4=Xticl4(i,1)

Xehcl=Xhcl(i,1)

201 q=p/760.0

T0=298.15

T=Ts(i)+T0

DT=T-T0

DT2=T**2-T0**2

DT3=T**3-T0**3

DTM1=1.0/T-1.0/T0

DTM2=1.0/T/T-1.0/T0/T0

DLNT=ALOG(T)-ALOG(T0)

DLNT2=ALOG(T)**2-ALOG(T0)**2

DTLNT=T*ALOG(T)-T0*ALOG(T0)

DHch4=((-1.7895e+1)+(-7.70678e-2)*DT+(-3.93376e-6)*DT2/2.-

& (5.57928e+2)*DTM1+(1.41329e-2)*(DTLNT-DT))

DEch4=((-1.9306e-2)+(-7.70678e-2)*DLNT+(-3.93376e-6)*DT-

& (5.57928e+2)*DTM2/2.+(1.41329e-2)*DLNT2/2.)

DGch4= DHch4-T*DEch4

DHticl4=((-1.824e+2)+(9.53274e-3)*DT+(-1.37046e-6)*DT2/2.-

& (-5.03346e+1)*DTM1+(2.51482e-3)*(DTLNT-DT))

DEticl4=((-2.91655e-2)+(9.53274e-3)*DLNT+(-1.37046e-6)*DT-

& (-5.03346e+1)*DTM2/2.+(2.51482e-3)*DLNT2/2.)

DGticl4= DHticl4-T*DEticl4

DHHcl=((-2.2063e+1)+(5.8700e-3)*DT+(2.000e-6)*DT2/2.+

& (-3.4300e-10)*DT3/3.-(-4.9600e+1)*DTM1)

DEhcl=((2.3945e-3)+(5.8700e-3)*DLNT+(2.000e-6)*DT+

& (-3.4300e-10)*DT2/2.-(-4.9600e+1)*DTM2/2.)

DGhcl=DHHcl-T*DEhcl

DHtic=((-4.4000e+1)+(1.2300e-2)*DT+(-2.9400e-7)*DT2/2.+

& (6.2800e-10)*DT3/3.-(-3.7600e+2)*DTM1)

DEtic=((-2.9326e-3)+(1.2300e-2)*DLNT+(-2.9400e-7)*DT+

& (6.2800e-10)*DT2/2.-(-3.7600e+2)*DTM2/2.)

DGtic=DHtic-T*DEtic

Ek=exp((DGch4+DGticl4-DGtic-4.0*DGhcl)/((1.9872e-3)*T))

c

c--- Newton-Raphson Routine to Find Xhcleq -----

c

G=(-0.5)/(3.0-(4.0/Xehcl))

202 DF=((256.0)-(4.0*Ek/q**2))*(4.0*G**3)+((256.0*Xehcl)-(4.0*Ek/q**2)

& *(1.0-Xech4-Xeticl4))*(3.0*G**2)+((96.0*Xehcl**2)-(Ek/q**2)*

```

& (4.0*Xech4*Xeticl4-4.0*Xech4-4.0*Xeticl4+1.0))*(2.0*G)+
& ((16.0*Xehcl**3)-(Ek/q**2)*(4.0*Xech4*Xeticl4-Xech4-Xeticl4))
Fo=((256.0)-(4.0*Ek/q**2))*(G**4)+((256.0*Xehcl)-(4.0*Ek/q**2)*
& (1.0-Xech4-Xeticl4))*(G**3)+((96.0*Xehcl**2)-(Ek/q**2)*
& (4.0*Xech4*Xeticl4-4.0*Xech4-4.0*Xeticl4+1.0))*(G**2)+
& ((16.0*Xehcl**3)-(Ek/q**2)*(4.0*Xech4*Xeticl4-Xech4-Xeticl4))
& *(G)+((Xehcl**4)-(Ek/q**2)*(Xech4*Xeticl4))
Gn=G-(Fo/DF)
G=Gn
Fn=((256.0)-(4.0*Ek/q**2))*(G**4)+((256.0*Xehcl)-(4.0*Ek/q**2)*
& (1.0-Xech4-Xeticl4))*(G**3)+((96.0*Xehcl**2)-(Ek/q**2)*
& (4.0*Xech4*Xeticl4-4.0*Xech4-4.0*Xeticl4+1.0))*(G**2)+
& ((16.0*Xehcl**3)-(Ek/q**2)*(4.0*Xech4*Xeticl4-Xech4-Xeticl4))
& *(G)+((Xehcl**4)-(Ek/q**2)*(Xech4*Xeticl4))
if(abs(Fn).ge.abs(Fo))then
  write(*,*) 'Newton-Raphson routine did not converge'
  write(*,*) '(time)j=j,'(z)i=i,'(r)m=m',m
  go to 700
else
  if(Abs(Fn).lt.1e-10)then
    if(G.lt.0.0) go to 202
    Xhcleq=(Xohcl+4.0*G)/(1.0+2.0*G)
    go to 203
  else
    go to 202
  endif
endif
c
c-----
c
203 Resrch4(i)=Xhcleq(i)/k(i)
  Resmch4(i)=T0ch4(i)*(d(i)*(1e-6)/2.0)*((9.0*zl(i))**((1.0/3.0)))/
  & (C(i)*Dch4(i))
  Rx(i)=Xoch4/(Resrch4(i)+Resmch4(i))
  Rd(i)=Rd(i)+(tdis*Mw*Rx(i)/(den*Dp/2.0))
  d(i)=d(i)-(2.0*tdis*Mw*Rx(i)/den)
  qo=ij*tsto-t
  if(qo.eq.0) Rrd(i,ij)=Rd(i)
  if(qo.eq.0.and.i.eq.Nz+1) ij=ij+1
c
c--- Beginning of r-dir iteration loop -----
c
  Do 220 m=1,Nr+2
  if(i.ne.1) go to 223
  Txch4=0.0

```

```

Txicl4=0.0
Txhcl=0.0
go to 224
223 if(m.ne.Nr+2)go to 225
    rr=15
    go to 230
225 r=(dm(i)/Nr)*(m-1)
    rr=r/dm(i)
230 psi=rr/((9.0*zl(i))**(1.0/3.0))
    TXch4=T0ch4(i)
    TXticl4=T0ticl4(i)
    TXhcl=T0hcl(i)
c
c--- T(x) integral calculation loop -----
c
    nnu=1000
    dels=psi/nnu
    Do 240 ii=1,nnu
        ym=exp(-1.0*(((ii-1)*dels)**3)/alpch4(i))
        y=exp(-1.0*(((ii)*dels)**3)/alpch4(i))
        TXch4=TXch4-(dels)*(ym+y)/2.0
        ym=exp(-1.0*(((ii-1)*dels)**3)/alpticl4(i))
        y=exp(-1.0*(((ii)*dels)**3)/alpticl4(i))
        TXticl4=TXticl4-(dels)*(ym+y)/2.0
        ym=exp(-1.0*(((ii-1)*dels)**3)/alphcl(i))
        y=exp(-1.0*(((ii)*dels)**3)/alphcl(i))
        TXhcl=TXhcl-(dels)*(ym+y)/2.0
240 continue
c
c--- Mole fraction calculation
c
224 Xch4(i,m)=Xoch4-(((dm(i)*1e-6)/2)*((9.0*zl(i))**(1.0/3.0))*Rx(i)*
    & TXch4)/(Dch4(i)*C(i))
    Xticl4(i,m)=Xoticl4-(((dm(i)*1e-6)/2)*((9.0*zl(i))**(1.0/3.0))*
    & Rx(i)*TXticl4)/(Dticl4(i)*C(i))
    Xhcl(i,m)=Xohcl-(((dm(i)*1e-6)/2)*((9.0*zl(i))**(1.0/3.0))*Rx(i)*
    & TXhcl)/(Dhcl(i)*C(i))
220 continue
c
c-----
c
    if(j.ne.1)go to 221
    Xech4=Xch4(i,1)
    Xeticl4=Xticl4(i,1)
    Xehcl=Xhcl(i,1)

```

```

221 dm(i)=d(i)
200 continue
c
c--- Properties print statements for one time iteration and the ---
c--- whole length of the pore. -----
c
  to=it*tsto-t
  if(to.ne.0)go to 100
  it=it+1
  write(2,322)
  write(2,310) t
310 format('t= ',f10.1,' sec')
  write(2,322)
  write(2,320)
320 format('  Z/L    Ts    k    Dfch4    Dfticl4    Dfhcl
&    Dkch4')
  write(2,321)
321 format('          (oC) (mol/s.m2) (m2/s) (m2/s) (m2/s)
&    (m2/s)')
  write(2,322)
322 format(' ')
  do 323 ix=1,Nz+1
  write(2,325) zl(ix),Ts(ix),k(ix),Dfch4(ix),Dfticl4(ix),Dfhcl(ix),
&    Dkch4(ix)
323 continue
324 format(4(f8.6,2x),f11.5)
325 format(f8.6,2x,f8.1,2x,5(f8.6,2x))
  write(2,322)
  write(2,330)
330 format(' Dkticl4 Dkhcl    Dch4    Dticl4    Dhcl    C
&    U ')
  write(2,331)
331 format(' (m2/s) (m2/s) (m2/s) (m2/s) (m2/s) (mol/m3
&) (m/s) ')
  write(2,322)
  do 332 ix=1,Nz+1
  write(2,326) Dkticl4(ix),Dkhcl(ix),Dch4(ix),Dticl4(ix),Dhcl(ix),
&    C(ix),U(ix)
326 format(6(f8.6,2x),f10.5)
332 continue
  write(2,322)
  write(2,340)
340 format(' Alpch4    Alpticl4    Alphcl    T(0)ch4    T(0)ticl4 T(
&0)hcl')
  write(2,322)

```

```

do 341 ix=1,Nz+1
  write(2,327) alph4(ix),alpticl4(ix),alphcl4(ix),T0ch4(ix),
    &      T0ticl4(ix),T0hcl4(ix)
341 continue
327 format(3(f10.5,2x),3(f8.6,2x))
  write(2,322)
  write(2,350)
350 format(' Xhcleq  Resrch4  Resmch4  Rx      d  ')
  write(2,351)
351 format('      (m2.s/mol)(m2.s/mol)(mol/m2.s)  (um)  ')
  write(2,322)
  do 352 ix=1,Nz+1
    write(2,324) Xhcleq(ix),Resrch4(ix),Resmch4(ix),Rx(ix),d(ix)
352 continue
c
c--- Mole fraction print statements for one time iteration and ---
c--- the whole pore length and diameter.      ----
c
  write(3,322)
  write(3,310) t
  write(3,322)
  write(3,410)
410 format(' Xch4  Xch4  Xch4  Xch4  Xch4  Xch4
  &  Xch4')
  write(3,411)
411 format('r/R= 0      0.2      0.4      0.6      0.8      1.0
  &  15 ')
  write(3,322)
  do 412 ix=1,Nz+1
    write(3,413) (Xch4(ix,mx), mx=1,Nr+2)
412 continue
413 format(7(f8.5,2x))
  write(3,322)
  write(3,310) t
  write(3,322)
  write(3,420)
420 format(' Xticl4  Xticl4  Xticl4  Xticl4  Xticl4  Xticl4
  &  Xticl4')
  write(3,411)
  write(3,322)
  do 422 ix=1,Nz+1
    write(3,413) (Xticl4(ix,mx), mx=1,Nr+2)
422 continue
  write(3,322)
  write(3,310) t

```

```

        write(3,322)
        write(3,430)
430 format(' Xhcl   Xhcl   Xhcl   Xhcl   Xhcl   Xhcl
      & Xhcl ')
        write(3,411)
        write(3,322)
        do 432 ix=1,Nz+1
            write(3,413) (Xhcl(ix,mx), mx=1,Nr+2)
432 continue
100 continue
c
c--- Deposition profile print statements for full deposition time ---
c--- and whole pore length and diameter.          ---
c
        nsp=Ns/7
        nspcr=Ns-7*nsp
        if(nspcr.ne.0) nsp=nsp+1
        do 500 j=1,nsp
            ne=7*j
            if(j.eq.nsp.and.nspcr.ne.0) ne=Ns
            nb=ne-6
            if(j.eq.nsp.and.nspcr.ne.0) nb=7*(j-1)+1
            write(4,510)
510 format('          Rrd   Rrd   Rrd   Rrd   Rrd
      & Rrd   Rrd ')
            t1=nb*tsto
            t2=(nb+1)*tsto
            t3=(nb+2)*tsto
            t4=(nb+3)*tsto
            t5=(nb+4)*tsto
            t6=(nb+5)*tsto
            t7=(nb+6)*tsto
            write(4,520) t1,t2,t3,t4,t5,t6,t7
520 format('t(sec)= ',7f9.1)
            write(4,322)
            do 550 i=1,Nz+1
                write(4,560) (Rrd(i,m), m=nb,ne)
560 format(9x,7f9.5)
550 continue
500 continue
700 end

```

BIOGRAPHICAL SKETCH

Roger Antonio Aparicio was born on February 18, 1965, in David, Panama. He graduated from Felix Olivares Contreras High School with valedictorian honors in December 1983. Following this, he attended Iowa State University to pursue a degree in chemical engineering. In the spring 1986, he was selected to represent the chemical engineering department in a semester honors exchange program at the University of Bradford, England. In May 1988, he received his B.S. in chemical engineering with honors from Iowa State University. In the fall of 1988, he enrolled in the chemical engineering graduate program at the University of Florida to pursue his doctoral degree.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



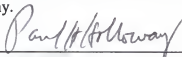
Timothy J. Anderson, Chairman
Professor of Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Michael D. Sacks
Professor of Materials Science and
Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Paul H. Holloway
Professor of Materials Science and
Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Raj Rajagopalan
Professor of Chemical Engineering

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.



Oscar D. Crisalle
Associate Professor of Chemical
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This dissertation was submitted to the Graduate Faculty of the College of Engineering and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 1997

A handwritten signature in dark ink, appearing to read 'W. M. Phillips', is written over a horizontal line.

Winfred M. Phillips
Dean, College of Engineering

Karen A. Holbrook
Dean, Graduate School